



### Attachments

**Declaration Under 37 CFR §1.132:** Declaration of Dr. M.J. Zaworotko.

**Exhibit A:** Dr. M.J. Zaworotko's Curriculum vitae

**Exhibit B:** References B1-B6.

- B1. B. Moulton & Zaworotko, M. "From Molecules to Crystal Engineering: Supramolecular Isomerism and Polymorphism in Network Solids." *Chem Rev.* 2001, 101, 1629-58.
- B2. B. Moulton; Lu, J.; Mondal, A.; & Zaworotko, M. "Nanoballs: nanoscale faceted polyhedra with large windows and cavities." *Chem. Commun.*, 2001, 863-64.
- B3. B. Moulton; Lu, J.; Hajndl, R.; Hariharan, S.; & Zaworotko, M. "Crystal Engineering of a Nanoscale Kagomé Lattice." *Angew. Chem. Int. Ed.* 2002, 41, No. 15.
- B4. Abourahma, H.; Coleman, A.; Moulton, B.; Rather, B.; Shahgaldian, P.; & Zaworotko, M. "Hydroxylated nanoballs: synthesis, crystal structure, solubility and crystallization on surfaces." *Chem. Commun.*, 2001, 2380-2381.
- B5. Bourne, S.; Lu, J.; Mondal, A.; Moulton, B.; & Zaworotko, M. "Self-Assembly of Nanometer-Scale Secondary Building Units into an Undulating Two-Dimensional Network with Two Types of Hydrophobic Cavity." *Angew Chem. Int. Ed.* 2001, 40, 2111-13.
- B6. McManus, G. J.; Wang, Z.; Zaworotko, M. "Suprasupermolecular Chemistry: Infinite Networks from Nanoscale Metal-Organic Building Blocks," *Crystal Growth & Design*, 4, 11-13, 2004.

**Exhibit C:** Reference C1.

- C1. Chand, D.K.; Biradha, K.; Fujita, M.; Sakamoto, S.; and Yamaguchi, K. "A molecular sphere of octahedral symmetry," *Chem. Commun.* 2002, 2486-2487.



Patent Application  
Docket No. USF-104XC1  
Serial No. 10/083,781

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Examiner : Nathan M. Nutter  
Art Unit : 1711  
Serial No. : 10/083,781  
Conf. No. : 5476  
Filed : February 25, 2002  
Applicants : Michael J. Zaworotko, Brian Moulton  
For : Nanoscale Faceted Polyhedra

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

DECLARATION OF MICHAEL J. ZAWOROTKO, Ph.D., UNDER 37 CFR 1.132

Sir:

I, Michael J. Zaworotko, hereby declare:

THAT, I am a co-inventor of the subject matter claimed in U.S. patent application Serial No. 10/083,781 (hereinafter the '781 application);

THAT, a copy of my curriculum vitae is attached hereto;

THAT, I have reviewed the Office Action mailed April 22, 2004, in the '781 application along with the references cited therein;

THAT, by virtue of my employment, my educational background, my research, my participation in authoring and reviewing articles and publications, my attendance at and participation in conferences and seminars, and my personal correspondence with others in the field, I am aware of the level of skill of the ordinary artisan in the field of nanoscale materials.

And, being thus duly qualified, do further declare as follows:

I. The subject invention is based on molecular faceted polyhedra. Faceted polyhedra are molecular polygons linked at their vertices. A linking moiety provides the connection between the molecular polygons and subtends the angle between the planes of the linked polygons.

connection between the molecular polygons and subtends the angle between the planes of the linked polygons.

II. The Office Action states that the subject application does not enable one skilled in the art to make and use the entire scope of the claimed invention without undue experimentation. As a co-inventor and an expert in this field, the undersigned submits that the subject application adequately teaches the full scope of the claimed invention to one having ordinary skills in the art who, with knowledge of the prior art on February 25, 2002, and in view of the teachings of our specification, could make and use our invention to the full extent of the claims. The ordinary skilled artisan would understand that faceted polyhedra applies to a multitude of molecular polygons and linking moieties, all of which are readily available to the ordinary artisan and can be assembled into the faceted polyhedra that we teach.

The application provides attributes that give adequate direction in how to choose appropriate molecular polygons and linking moieties depending on, for example, the type of geometric shape desired or whether the polygon molecule should contain a metal. As taught in the application, the components of the molecular polygons are those capable of sustaining the desired rotational symmetry. Although an illustrative list of these types of metals and non-metals are given, one skilled in the art would understand that any type of metal or nonmetal could be used as long as the rotational symmetry requirement is met. Additionally, the application teaches that the linking molecules are selected to sustain a desired dihedral angle between the molecular polygons as well as proving illustrative lists. Thus, the skilled artisan is not limited to merely making and using just the faceted polyhedra specified in the examples. In fact, as more fully explained below, a number of those skilled in the art have successfully followed our teachings to produce non-exemplified faceted polyhedra, thereby proving the broadly-enabled character of our teachings.

Geometry teaches us that *faceted polyhedra* can only be generated from certain polygons or combinations of polygons. We have demonstrated by our examples and publications that molecular squares that are linked at a 120 degree angle self-assemble (*i.e.* a spontaneous one-pot chemical process) to form one of the nine possible faceted polyhedra: the small

rhombihexahedron. To our knowledge this represents the first example of such a chemical structure. In the application and the papers we demonstrate that a series of metal-organic moieties that approximate the shape of squares can be linked by angular "spacers" (iso-phthalic acid and several of its derivatives) to generate a molecular scale version of the small rhombihexahedron. Our results mean that it would be obvious to anyone skilled in the art how one could use other molecular squares, triangles or pentagons (three polygons that can sustain faceted polyhedra) linked by other angular "spacers" to generate the full series of faceted polyhedra. In particular, the following support both the generality and potential importance of this class of compounds:

- They will be based upon previously reported molecular species and will thereby be facile and typically inexpensive to synthesize.
- Our structures can be afforded via self-assembly meaning that they can be prepared in one-step with high yield.
- The nature of self-assembly is that products are inherently modular since they contain at least two components, affording diversity of compositions since both the polygon and the spacer can be modified without loss of overall topology.
- Many of the compounds described herein are stable to 200°C and others are stable at or above 400°C.
- Modular compounds can be designed so as to contain at least two chemically active components. For example, a metal complex or organic molecule could be chosen for luminescence or molecular recognition properties as well as its structural features, and metal complexes could be selected for magnetic or catalytic properties.
- Components could be neutral or ionic and the faceted polyhedra could therefore also be designed to be ionic or neutral.

Several articles authored in part by the co-inventors provide further evidence that the application is enabling for the full extent of the claims. The list of publications includes:

B1. B. Moulton & Zaworotko, M. "From Molecules to Crystal Engineering: Supramolecular Isomerism and Polymorphism in Network Solids." *Chem Rev.* 2001, 101, 1629-58.

B2. B. Moulton; Lu, J.; Mondal, A.; & Zaworotko, M. "Nanoballs: nanoscale faceted polyhedra with large windows and cavities." *Chem. Commun.*, 2001, 863-64.

B3. B. Moulton; Lu, J.; Hajndl, R.; Hariharan, S.; & Zaworotko, M. "Crystal Engineering of a Nanoscale Kagomé Lattice." *Angew. Chem. Int. Ed.* 2002, 41, No. 15.

B4. Abourahma, H.; Coleman, A.; Moulton, B.; Rather, B.; Shahgaldian, P.; & Zaworotko, M. "Hydroxylated nanoballs: synthesis, crystal structure, solubility and crystallization on surfaces." *Chem. Commun.*, 2001, 2380-2381.

B5. Bourne, S.; Lu, J.; Mondal, A.; Moulton, B.; & Zaworotko, M. "Self-Assembly of Nanometer-Scale Secondary Building Units into an Undulating Two-Dimensional Network with Two Types of Hydrophobic Cavity." *Angew Chem. Int. Ed.* 2001, 40, 2111-13.

B6. McManus, G. J.; Wang, Z.; Zaworotko, M. "Suprasupermolecular Chemistry: Infinite Networks from Nanoscale Metal-Organic Building Blocks", *Crystal Growth & Design*, 4, 11-13, 2004.

Copies of these six articles are provided in Exhibit B, attached hereto. In the course of our research on faceted polyhedra, Mr. Brian Moulton and I have been assisted to varying degrees by several people, including Jianjiang Lu, Arunendu Mondal, Ranko Hajndl, Srikanth Hariharan, Heba Abourahma, Anthony W. Coleman, Beth Rather, Patrick Shahgaldian, Susan A. Bourne, Gregory J. McManus, and Zhenqiang Wang. These individuals were included as co-authors with Mr. Moulton and myself on the above-referenced publications. Although their efforts were greatly appreciated and, accordingly, they were acknowledged as co-authors on the above publications, they did not contribute to the conception of the claimed invention. Therefore, despite their helpful research assistance and input, they were not included as co-inventors on the subject application.

The above-referenced articles contain much of the same teachings as the subject application, have been highly cited since their publication, and thereby have taught others possessing ordinary skills in the art to make and use the claimed invention. In particular, B1 was named the "hot paper for chemistry" by the Institute for Scientific Information in June 2003 since it had been cited 244 times within two years of publication, the most of any chemistry article published in this time period (June 2001-June 2003). As of August 2004, this article has

been cited 574 times. Some of these articles have also been featured in other esteemed scientific journals. B2 is an Editor's Choice in the May 18, 2001 issue of *Science*, and B3 was highlighted in the News and Views section of *Nature Materials* in their October 2002 issue.

Not only did B2 and B3 gain additional publicity in the above journals, these articles have been used and cited in over 25 articles each. A full text copy of one such article is given in Exhibit C, attached hereto.

Thus, in view of these publications in the field showing success in following our teachings, the disclosure of the subject invention enables another skilled in the art to make and use the claimed invention.

III. The Office Action also finds the claimed invention indefinite. However, the terminology of the claims is consistent with the terminology used by one ordinarily skilled in the art. The term "faceted uniform polyhedra" is defined in the specification of the subject application as "[t]he resulting nine closed sets of polygons that are sustained by vertex-linked triangles, squares, pentagons, or combinations thereof, . . ." This term has consistently been used in publications since 2001.

Furthermore, the other elements of the faceted polyhedra are defined in the specification or known to someone skilled in the art. For example, the term "polygon moiety" is defined in the application as a "polygon-shaped moiety which contribute[s] to the polyhedron molecules and polymeric structures of the subject invention." Someone of ordinary skill in the art understands that the moieties' arrangement of atoms approximate geometric structures.

Likewise, the term "linking moiety" is known in the chemical arts. Additionally, the application specifically defines what is meant by linking moieties in the context of the claimed invention in paragraphs 95-97.

Thus, the claimed invention does define the bounds of the claimed invention using terms well known within the art and defined in the subject application.

IV. The Office Action also maintains that the claimed invention is not novel over Spencer *et al.* (Patent No. 6,531,107) and Seeman *et al.* (U.S. Patent No. 6,072,044). After analyzing these

references, it is clear that neither teaches a faceted polyhedra or polymeric structure as is claimed in our application.

Spencer *et al.* fails to teach a faceted polyhedra molecule wherein the molecule has open and closed convex faces. Spencer *et al.* teaches cluster frameworks, for example, borane and carboborane, wherein polygons are connected at their edges. As known to one skilled in the art, when polygons are linked at their edges, a closed polyhedra is prepared.

In contrast, the faceted polyhedra of the claimed invention has both open and closed faces, thus it is faceted. The open faces are prepared by linking polygon moieties polygons at their vertices with a linking moiety. As defined in the specification, polygon moieties are those moieties with external chemical functionalities that are arranged in such a way that the functionalities lie at the vertices of the polygon. Thus, Spencer *et al.* fails to teach a polyhedra with both open and closed faces.

Seeman *et al.* discloses two and three dimensional polynucleic acid structures. The Seeman structures are constructed of ordered arrays of antiparallel double crossover molecules.

The vertices of the Seeman lattices are bulges from the nucleic acids rather than individual polygon moieties. In contrast, the polygon moieties of my invention are polygon moieties with vertices having external chemical functionalities that are arranged in such a way that the functionalities lie at the vertices of the polygon.

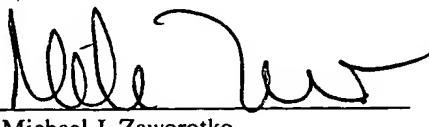
Furthermore, the nanoconstructions disclosed in Seeman *et al.* do not teach faceted polyhedra molecules or structures. As noted above, faceted polyhedra molecules are defined in paragraph 84 as a set of polygons connected at their vertices and having both open and closed faces. In contrast, the nanostructures of Seeman as seen in Figures 11A, 11B, and 13 contain closed faces. Furthermore, these structures are connected at their edges. Thus, Seeman *et al.* fails to teach polygon moieties connected at their vertices by a linking moiety.

The undersigned declare further that all statements made herein of his or her own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section

1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or of any patent issuing thereon.

Further declarant sayeth naught.

Signed:



\_\_\_\_\_  
By: Michael J. Zaworotko

Date:

08/20/04

# CURRICULUM VITAE

## MICHAEL JOHN ZAWOROTKO

**Date of Birth:** 14 August, 1956, Tredegar, South Wales

**Citizenship:** United Kingdom and Canada (Dual Citizen)  
Permanent resident of USA

**Address:** Department of Chemistry  
University of South Florida  
SCA400, 4202 E. Fowler Avenue  
Tampa, Florida, 33620-5250, USA  
Ph: (813) 974 4129 FAX: (813) 974 3203  
Home phone: (813) 857 8322  
e-mail:"xtal@usf.edu"

## EDUCATION

**1974 - 77** Imperial College, London, U.K.  
B.Sc. (Hons), A.R.C.S.

**1978 - 82** University of Alabama  
Ph.D. (supervisor: J.L. Atwood)

## EMPLOYMENT

**1979 - 82** University of Alabama  
Research Assistant (Biology Department)

**1982 - 85** University of Victoria  
Post-Doctoral Fellow (S.R. Stobart)

**1985 - 89** Saint Mary's University  
Assistant Professor

**1989 - 95** Saint Mary's University  
Associate Professor

**1991 - 92** NRC Senior Research Associate (U.S.)  
- Sabbatical Leave, USAF Academy

**1994-97** Saint Mary's University  
Chairperson, Department of Chemistry

**1995-97** Saint Mary's University, Professor

**1995-99** President, Diazans Limited

**01/98-09/99** Dean of Arts and Science, University of Winnipeg

**09/99-present** Chair, Department of Chemistry,  
University of South Florida

## **RESEARCH AND SCHOLARLY ACTIVITIES**

My research activities are quite broad and multidisciplinary as they encompass my interests in synthesis (organic and metal-organic), noncovalent bonding (hydrogen bonding,  $\pi$ -stacking), and X-ray crystallography. I have thus far obtained funding from both industrial (Imperial Oil, Institute for Chemical Science and Technology, Shaw Group Limited, Manitoba Livestock Manure Management Initiative, Transform Pharma, Bausch and Lomb) and government sources (NSERC, NATO, IRAP, NSF). The long range objectives of my program involve fundamental and targeted research into design and synthesis of novel nanoscale materials using the principles of self-assembly and crystal engineering. Specific functions will be targeted e.g. molecular recognition ("third generation" liquid clathrate sustaining salts/ ionic liquids and novel organometallic "supramolecules", microporous solids) and crystal engineering of solids with important functional properties (e.g. 1-D conductors, nonlinear optics, porosity, pharmaceuticals). My program has thus far involved active participation by undergraduate students, graduate students, research technicians and post-doctoral fellows and typically sustains a group of seven to twelve researchers. My teaching activities have focussed around my specialty, inorganic chemistry, although I have introduced new courses in other areas (organic spectroscopy, organometallic chemistry).

#### **Honours and Awards:**

NRC Senior Research Associate (U.S. Air Force Academy), 1992; President's Award for Research Excellence, Saint Mary's University, 1994; Honorary Member of the Academy of Science of Higher School of Ukraine, 1998; Visiting Professor, Universite Louis Pasteur, Strasbourg, 1999; Visiting Professor, Institute of Biology and Chemistry of Proteins, CNRS, Lyon, France, 2001; Conference Universitaire de Suisse Occidentale Lecturer, 2002.

#### **Membership in Professional Organizations:**

1982 - present American Chemical Society

### **Research Grants Awarded:**

- 1986 . "Organotransition Metal Sustained Liquid Clathrates."  
NSERC Operating - \$16,320 - one year.

  - . "Liquid Clathrates - Utilization as Alkylating Agents  
NSERC Research Development - \$12,000/yr. - two years.
  - . "Metal Superoxide Complexes"  
NSERC General - \$4,000 - one year
  - . "Homogeneous Catalysis using Liquid Clathrates"  
Senate Research - \$1,500 and \$1,450 - one year.
  - . SEED Summer Employment Subsidy - ca. \$2,800

1987 . "Organotransition Metal Sustained Liquid Clathrates"  
NSERC Operating - \$16,320 - one year.

  - . "Determination of the Alkylating Capabilities of Anionic Petroleum Research Fund (type B) - U.S. \$10,000/yr. - two years.
  - . "Room Temperature Ionic Liquids"  
NSERC General - \$2,500 - one year.
  - . "Novel Applications of Liquid Clathrates"  
Senate Research - \$1,756 - one year.
  - . SEED Summer Employment Subsidy - ca. \$1,500.

1988 . "Salt Sustained Liquid-Liquid Binary Phases"  
NSERC Operating - \$10,000 - one year.

  - . "Novel Approaches to Hydrocarbon Separation Problems"  
Imperial Oil Ltd. (URG) - \$10,000 - one year.
  - . "Applications of Room Temperature Liquids"  
NSERC General - \$4,000 - one year.
  - . "Applications of Ionic Liquids to Separation Problems"  
Senate Research - \$1,600 - one year.

- SEED Summer Employment Subsidy - ca. \$2,000
- 1989 . "Aspects of Arene Chemistry"
  - NSERC Operating - \$25,844 per year for 3 years.
  - "Hydrocarbon Separation Properties of Molten Salts"
    - Imperial Oil Ltd. (URG) - \$8,000 - 1 year.
  - "Novel Approaches to Lubricating Oil Processing"
    - NSERC University/Industry with Imperial Oil - \$50,000 per year
- 1990 . An internal grant of \$116,000 was awarded for purchase of
- 1991 . "X-ray crystallographic work station"
  - NSERC Equipment - \$25,193.
- 1992 . "Arenes: Covalent and Non-covalent Bonding"
  - NSERC operating - \$26,810 per year for four years.
  - "Ionic Liquids"
    - NSERC General - \$2,500
- 1993 . "Crystal Engineering of Diamondoid Networks with Zeolite-Like Physical Features"
  - NSERC University/Industry with ICST - \$60,000 - 1 year.
- 1994 . "Crystal Engineering of Microporous Polymeric Solids"
  - ICST and NSERC - \$89,000/year - 2 years.
- 1995 . "Novel Biologically Active Compounds"
  - Contract from Shaw Group Ltd. - \$100,000 - 1 year
- 1995 . "Crystal Engineering: The Design and Application of Functional Solids"
  - NATO ASI - US\$80,000 (co-chair with K. Seddon)
- 1996 . "Crystal Engineering of Functional Solids"
  - NSERC - \$40,740 per year - 4 years
- 1996 . "Low temperature device for single crystal X-ray diffractometer"
  - NSERC Equipment - \$33,730.
- 1996 . "Novel Biologically Active Compounds"
  - Contract from Shaw Group Ltd. and IRAP - \$150,000 - 1 year
- 1996 . "Guest Interactions in Crystal Engineered Host Frameworks"
  - NATO CRG - \$11,300 (with K. Seddon, R. Rogers)
- 1996 . "Environmental Applications of Organic Clays"
  - ESTAC and NSERC - \$38,300 - 1 year
- 1996 . "CCD diffractometer"
  - Internal Research Grant - \$240,000
- 1998 . "Novel Technology for Hog Manure Remediation – \$35,000 – 1 year"
  - Manitoba Livestock Manure Management Initiative
- 1998 . "Environmental Applications of Organic Clays" – \$75,000 – 1 year
  - ESTAC/NSERC (with M. Lamoureux, Saint Mary's university)
- 2000 . "Biocomposite Materials by Design" – \$20,000 – 1 year – Florida High Technology Corridor (with D. Merkler, University of South Florida)
- 2000 . "Characterization of Polymorphs of Fluocinolone Acetonide" - \$20,000 – 1 year
  - Bausch & Lomb Pharmaceuticals, Ltd., Tampa.
- 2001 . "From Molecular Polygons to Discrete Faceted Polyhedra to Porous Frameworks" – \$445,219 – 04/15/01 thru 03/31/04 – National Science Foundation (Division of Materials 0101641).
- 2001. "Synthesis, X-ray Study and Inclusion Properties of the Crown Based Extended Networks" - \$35,000 – 01/01/02 thru 04/30/03 – US Civilian Research and Development Foundation (with Y. Simonov, Moldova, 20% of funds to M.Z.)
- 2001. "Intelligent Design of Pharmaceutical Solids" - \$40,000 – 06/01/02 thru 05/31/03 – Vahlteich Research Fund (with N. Rodriguez, University of Michigan, 40% of funds to M.Z.).
- 2002. "Multi-Component Crystalline Pharmaceutical Phases" - \$35,000 – 01/01/03 thru 12/31/03 – Transform Pharmaceuticals

2003. "Integrated Interdisciplinary Nanoscience REU" – \$223,000 – 01/01/03-12/31/05 – National Science Foundation (PI with co-PI's R. Walsh and P. Muisener and 7 faculty mentors).
2003. "Molecular Nanoscience Research at USF – NanomolUSF" - \$50,000 – 05/01/03-04/30/05 – Interdisciplinary Research Grant Program at USF (PI with co-PI's S. Hariharan and R. Schlaf)
2003. "Multi-Component Crystalline Pharmaceutical Phases" - \$320,000 – 08/26/03 thru 08/25/07– Transform Pharmaceuticals
2003. "Novel Agricultural Chemical Formulations" - \$12,000 – 09/01/03 thru 08/31/04 – Florida High Tech Corridor

### **Invited Seminars**

- 1987
  - . Mount Allison University
  - . CANMET, Ottawa
  - . Imperial Oil Limited, Sarnia
  - . University of Waterloo
  - . Dalhousie University
- 1988
  - . Acadia University
  - . University of South Alabama
  - . University of Alabama
- 1989
  - . Northern Illinois University
  - . Brown University
- 1990
  - . University of Saskatchewan
  - . Dalhousie University
- 1992
  - . Imperial Oil Limited, Sarnia
  - . CANMET, Ottawa
  - . University of Alabama
  - . University of Mississippi
  - . Wright Laboratory, Dayton, Ohio
  - . Memorial University of Newfoundland\*
  - . Dalhousie University\*
  - . University of New Brunswick\*
  - . Universite Moncton\*
  - . University of Prince Edward Island\*
  - . Mount Allison University\*
  - . University of Guelph
  - . University of Groningen
  - . University of Alabama
- 1994
  - . Acadia University
  - . University of Northern British Columbia
  - . Exxon Research and Engineering, N.J.
- 1995
  - . ETH Zurich
  - . The Queen's University of Belfast
  - . The University of Birmingham
  - . The University of Western Ontario
  - . The University of Windsor
- 1996
  - . Brown University
  - . Brown University
  - . Northern Illinois University
  - . National Research Council, Ottawa
  - . Trinity College, Dublin, Ireland
- 1997
  - . The University of Waterloo
  - . CNRS, Lyon, France
  - . University of Siegen, Germany
  - . Saint Mary's University

- . The University of Winnipeg
- . The University of Manitoba
- . Sumi State University
- . Institute of Physics of Ukraine
- . Kyiv State University
- . Trojan Technologies, London, Ontario
- . Nortran Pharmaceuticals, Vancouver
- . Apotex, Winnipeg
- . The University of Missouri, Columbia
- . The University of Manitoba (Physics)
- . Seoul National University, Korea
- . POSTECH, Pohang, Korea
- . University of South Florida
- . Universite Louis Pasteur, Strasbourg, France
- . Eastman Chemical, US
- . Bell Labs
- . University of Windsor, Canada
- . Constellation Technologies, Florida
- . Memorial University of Newfoundland, Canada
- . Acadia University, Canada
- . Mount Allison University, Canada
- . Saint Mary's University, Canada
- . University of Miami
- . University of Florida
- . Ckemson University
- . University of Alabama
- . University of Mississippi
- . University of South Carolina
- . University of Prince Edward Island, Canada
- . Saint Francis Xavier University, Canada
- . University of Michigan
- . Universite Claude Bernard, Lyon, France
- . University of Winnipeg, Canada
- . University of South Florida, College of Medicine
- . University of Iowa
- . University of North Carolina
- . Worcester Polytechnic Institute
- . Transform Pharmaceuticals
- . University of Durham, England
- . University of Geneva, Switzerland
- . University of Neuchatel, Switzerland
- . University of Fribourg, Switzerland
- . University of Bern, Switzerland
- . University of Winnipeg, Canada
- . University of Brandon, Canada
- . World Precision Instruments, Sarasota
- . University of South Florida, Complex Systems Seminar Series
- . University of Manitoba
- . University of Prince Edward Island
- . Mount Allison University
- . Saint Mary's University
- . Georgetown University
- . Institute for Chemical and Engineering Sciences, Singapore

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## **SYNERGISTIC ACTIVITIES:**

- Industrial interaction since 1992. Funded research with the following companies since 2000: Bausch and Lomb Pharma; Constellation Technologies; Breed Technologies; Transform Pharma; United Agricultural Services.
- Organizer of 12 symposia or conferences in U.S./Canada.
- 1999-present. Member of UTEK Corporation's Scientific Advisory Council, 2003-present Member of Transform Pharmaceutical Scientific Advisory Board.
- Founding Editor of *Crystal Engineering*, published by Elsevier; Editorial Board *CrystEngComm*, *J. Chemical Crystallography*, *Crystal Growth & Design*; International Advisory Committee, VIII International Seminar on Inclusion Compounds.
- Papers reviewed for many journals including *Science*, *Nature*, *JACS*, *Angewandte Chemie* in 2003.
- Invited participant in *Challenges for the Chemical Sciences in the 21<sup>st</sup> Century* workshop organized by NRC, 2002.
- Served on nanotechnology panels for Canadian Foundation for Innovation and NSF/EPSCOR in 2003.
- Cover art for *Crystal Growth & Design* (2004), *Chemical Communications* (2001), *Chemical Reviews* (2001).
- External Reviewer for the Following Theses: M.S. (Memorial University, 1990; University of Cape Town, 1996). Ph.D. (Saskatchewan, 1990; Alabama, 1993, Waterloo, 1997; Chinese University of Hong Kong, 1999; University of Windsor, 1999. University of Hyderabad, 2003).

**Zaworotko Group Members (Feb. 2004):** 9 Graduate students (B. Rather, H. Abourahma, J. Lu, G. McManus, R. Wong, J. McMahon, T. Shattock, J. Bis, J. Perry). 1 Postdoctoral (Dr. V. Kravstov).

## **ADMINISTRATIVE EXPERIENCE:**

**09/94-12/97: Chair, Department of Chemistry, Saint Mary's University.**

**Highlights:** academic leadership of Department at a time of faculty renewal and growth in majors and external funding.

**01/98-09/99: Dean of Arts and Science, University of Winnipeg.**

**Highlights:** administrative leadership for 90% of faculty and programs at University of Winnipeg, responsible for strategic resource allocation within College of Arts and Science.

**09/99-present: Chair, Department of Chemistry, University of South Florida.**

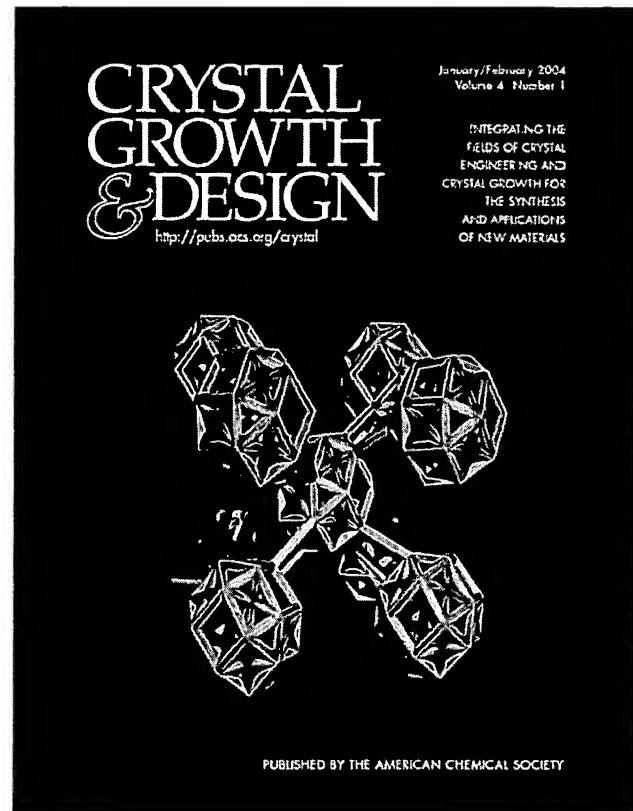
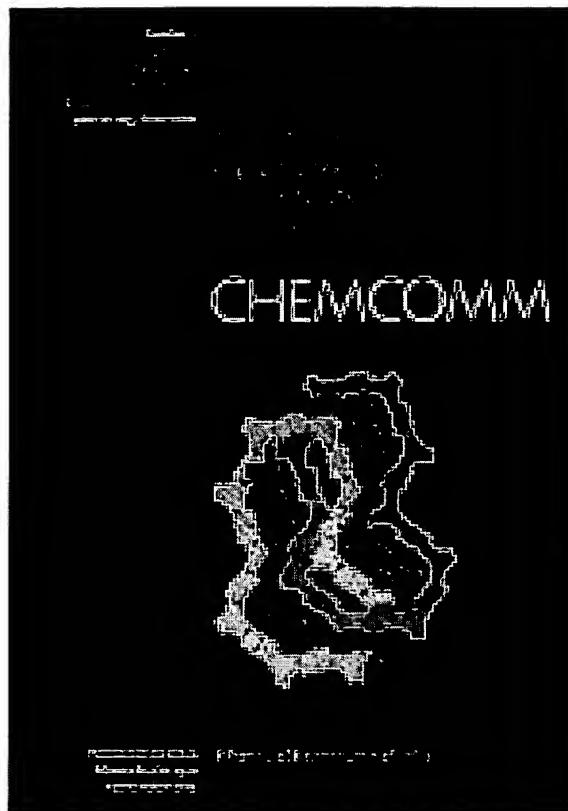
**Highlights:** Accountable officer for a Department in one of the 20 largest universities in the U.S. (currently >42,000 students). Department currently graduates ca. 100 majors per year, serves 90 graduate students and has 23 faculty and 12 staff. Developed a 5-year plan that has resulted in the hire of 10 new faculty since 1999. Departmental research grants now ca. \$3,000K/year (up from ca. \$400K/year in 1999). Responsible for fund raising and external relations.

## **EVIDENCE OF IMPACT:**

Evidence that our work has achieved impact is suggested by the quality of the journals in which we have published and the following:

- invited lectures at 17 regional, national or international meetings from 01/01 thru 02/04;
- invited seminars at 18 universities (US, Canada, UK, France, Switzerland) and 3 companies from 01/01 thru 02/04;
- well over 3000 citations since 01/99 including a 2001 review article which was determined by ISI to be the #1 hot paper in Chemistry in July 2003 and a 2001 hot paper in *Angewandte Chemie*;
- 15 publications since 1992 with >100 citations;
- featured in a *C&E News* article on metal-organic materials (09/15/03);
- featured as an Editor's Choice in *Science* (May 18th 2001, vol. 292, pg. 1293);
- featured in a *Nature Materials* News and Views article (October 2002, vol. 1, pgs. 91-92);
- my first Ph.D. student from University of South Florida has recently assumed a faculty position at an Ivy League school (Dr. Brian Moulton, Brown);

- two of my former honors students are now faculty members with NSF Career Awards (Dr. Len MacGillivray, Iowa; Dr. K. Travis Holman, Georgetown);
- Cover art for Crystal Growth & Design (2004), Chemical Communications (2001), Chemical Reviews (2001)



## PUBLICATIONS

C = Communication; F = Full Paper; N = Note; P = Patent; R = Refereed Conference Proceedings.; I = Invited Review or Highlight Article. Senior Author is underlined.

1. (C) Guzman, C.E.; Wilkinson, G; Atwood, J.L.; Rogers, R.D.; Hunter, W.E.; Zaworotko, M.J. "Synthesis and Crystal Structures of Chloro(trimethylphosphine)tris(trimethylsilylmethyl) molybdenum(IV) and Di- $\mu$ -chloro-bis[bis(carbonyl)tri-methylphosphine(1-2- $\eta$ -trimethylsilylmethyl-carbonyl)molybdenum (II)]." *J. Chem. Soc., Chem. Comm.*, 465, 1978.
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8. (F) Guzman, E.C.; Wilkinson, G.; Rogers, R.D.; Hunter, W.E.; Zaworotko, M.J.; Atwood, J.L. "Synthesis and Crystal Structures of Chloro (trimethylphosphine) tris(trimethylphosphine)(1-2-trimethyl-silylmethyl-carbonyl)molybdenum (II)." *J. Chem. Soc. Dalton Trans.*, 229, 1980.
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### Conference Presentations (excluding presentations by co-workers)

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2. Zaworotko, M.J.; Hrincir, D.; Shakir, R.; Atwood, J.L. "Comparison between Selected Trimethylaluminum and Trimethylgallium Based Liquid Clathrates." Presented by M.J. Zaworotko before the Meeting, 1980, New Orleans, Abstract 280.
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4. Bushnell, G.W.; Fjeldsted, D.O.K.; Stobart, S.R.; Vefghi, R.; Zaworotko, M.J. "Isolation of Novel Dimeric Iridium Structures through Two-centerOxidative Addition to Bis(1,5-cyclooctadiene)di( $\mu$ -pyrazolyl) Di-iridium(I)." Presented by M.J. Zaworotko before the 11th International Conference on Organometallic Chemistry, 1983, Pine Mountain, Georgia.
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10. Clerk, M.D.; Hooper, D.L.; Zaworotko, M.J. "Fluxional Properties of Sterically Crowded Sandwich Compounds." Presented by M.J. Zaworotko before the 72nd Canadian Chemical Conference, 1989, Victoria.
11. Zaworotko, M.J.; Sturge, K.C.; Clerk, M.D. "Effect of Transition Metal Complexation Upon Conformation and Reactivity of Arenes." **Invited talk** presented by M. J. Zaworotko before the CIC Atlantic Section Annual General Meeting and Conference, 1989, St. John's.
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18. Copp, S.B.; Subramanian, S.; Zaworotko, M.J. "Supramolecular Chemistry of  $[\text{Mn}(\text{CO})_3(\mu_3\text{-OH})]_4$ : Coassembly of Hydrogen Bonded Diamondoid Networks" Presented by M.J. Zaworotko before the Fall Materials Research Society Meeting, Boston, MA, December 1992.
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23. Zaworotko, M.J. "Aspects of Noncovalent Bonding". **Keynote speaker** at the 1995 Atlantic CIC Student Conference, Halifax, May 1995.
24. Zaworotko, M.J. "Molecular Recognition in Solids: Cocrystals by Design". **Invited talk**, 78th Canadian Chemical Conference, May 1995, Guelph, Ontario.
25. Zaworotko, M.J. "From Molecules to Crystals". **Invited lecture**, NATO ARW on Modular Chemistry, September 1995, Estes Park, Colorado, USA.

26. Zaworotko, M.J. "Crystal Engineering of Functional Solids". **Invited lecture**, ESTAC annual meeting, November 1995, Toronto, Canada.
27. Zaworotko, M.J. "Non-interpenetrated Molecular Ladders". **Invited poster**, NATO ARW on Modular Synthesis, May 1996, Montreal, Canada.
28. Zaworotko, M.J. "Chains, Planes and Frames: Crystal Engineering of Transition Metal Sustained Coordination Polymers". **Invited lecture**, 5<sup>th</sup> International Summer School on Supramolecular Chemistry, June 1996, Ustron Poland.
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35. Zaworotko, M.J. "Faculty Entrepreneurship: The Saint Mary's Experience". Canadian Research Management Association, September 1997, Halifax.
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41. Zaworotko, M.J. "The importance of weak hydrogen bonds in the context of the architectures adapted by coordination polymers". **Invited Lecture**, Boston ACS Meeting, August 1998.
42. Zaworotko, M.J. "From Molecules to Crystals". **Invited Lecture**, Gordon Conference on Organic Structures and Properties, September 1998, Fukuoka, Japan.
43. Zaworotko, M.J. "From Molecules to Crystals and Back Again". **Invited Lecture**, Materials Research Society Meeting, December 1998, Boston.
44. Zaworotko, "Crystal Engineering of Functional Solids". **Invited Lecture**, 62<sup>nd</sup> Okazaki conference, January 1999, Okazaki, Japan.
45. Zaworotko, M.J. "Strategies for the Design of Chiral Solids". **Invited Lecture**, PRESTO/FR Symposium on "Construction and Properties of Molecular Assemblies", January 1999, Okazaki, Japan.
46. Zaworotko, M.J. "Crystal Engineering of Functional Solids". **Invited Lecture**, Erice School on Crystallography/NATO-ASI, May 1999, Erice, Italy.
47. Zaworotko, M.J. "Zeolite and Clay Mimics: Design Strategies for Generation of Organic and Metal-Organic Adsorbents". **Invited Lecture**, Gordon Conference on Zeolites and Layered Materials, June 1999.
48. Zaworotko, M.J. "From Molecules to Crystals". **Invited Lecture**, Fourth International Conference on Materials Chemistry, Dublin, Ireland, July 1999.
49. Zaworotko, M.J. "From Achiral Building Blocks to Chiral Architectures", **Invited Lecture**, 18<sup>th</sup> Congress and General Assembly of the International Union of Crystallography, Glasgow, August 1999.
50. Zaworotko, M.J. "Novel Technology for Hog Manure Odour Control/Remediation", **Invited Lecture**, HEMS annual symposium, Ottawa, Canada, December 1999.

51. Zaworotko, M.J. "From Molecules to Crystals: Crystal Engineering and its Implication for Synthetic Chemistry", 17<sup>th</sup> Annual Florida Organic Chemistry Faculty Conference, Tampa, Florida, February 2000.
52. Zaworotko, M.J. "From Molecules to Crystals ... and Back Again". **Invited Lecture**, 10<sup>th</sup> Annual Meeting of the Association for Crystallization Technology, New Brunswick, New Jersey, April 2000.
53. Zaworotko, M.J. "Crystal Engineering of Zeolite and Clay Mimics". **Invited Lecture**, 83<sup>rd</sup> Canadian Society for Chemistry Conference, Calgary, Alberta, May 2000.
54. Zaworotko, M.J. "From Molecules to Crystals... and Back Again". 13<sup>th</sup> International Symposium on Surfactants in Solution, Gainesville, Florida, June 2000.
55. Zaworotko, M.J. "Design and Function of 2D and 3D Coordination Polymers". **Invited Lecture**, Royal Society of Chemistry, Dalton Discussion on Inorganic Crystal Engineering, Bologna, Italy, September 2000.
56. Zaworotko, M.J. "From Molecules to Crystals...and Back Again." **Keynote Lecture**. 1<sup>st</sup> International Workshop on Physical Characterization of Pharmaceutical Solids, Lancaster, PA, September 2000.
57. Zaworotko, M.J. "Coexisting Covalent and Noncovalent Nets". **Invited Lecture**, 35<sup>th</sup> ACS Midwest Regional Meeting, St. Louis, Missouri, October 2000.
58. Zaworotko, M.J. "Supramolecular Synthesis of Crystals". **Invited Lecture**, 35<sup>th</sup> ACS Midwest Regional Meeting, St. Louis, Missouri, October 2000.
59. Zaworotko, M.J. "Coexisting Covalent and Noncovalent Nets". **Invited Lecture**, ACS SW/SE Regional Meeting, New Orleans, Louisiana, December 2000.
60. Zaworotko, M.J. "Composite Materials by Design". **Invited Lecture**, Pacificchem 2000, Hawaii, December 2000.
61. Zaworotko, M.J. "Self-assembly of Discrete and Infinite Nanoscale Structures", **Invited Lecture**, AMRI-DARPA, New Orleans, February 2001.
62. Zaworotko, M.J. "Self-assembly of Discrete and Infinite Nanoscale Structures", **Invited Lecture**, XV International School-Seminar Spectroscopy of Molecular and Crystals, Chernihiv, Ukraine, June 2001.
63. Zaworotko, M.J. "Crystals and Nanocrystals by Design", **Invited Lecture**, ECM 20, "Supramolecular Materials Microsymposium", Krakow, Poland, August 2001.
64. Zaworotko, M.J. **Invited Lecture**, VIII International Seminar on Inclusion Compounds, Poland, September 2001.
65. Zaworotko, M.J. **Invited Lecture**, International Symposium on Crystal Chemistry, Chisinau, Moldova, October 2001.
66. Zaworotko, M.J. "From Molecules to Crystals: Crystal Engineering of Network Solids", **Invited Lecture**, 59<sup>th</sup> Pittsburgh Diffraction Conference, Cincinnati, October 2001.
67. Zaworotko, M.J. **Invited Lecture**, Modern Trends in Inorganic Chemistry, Calcutta, India, December 2001 (cancelled because of 9/11 related issues).
68. Zaworotko, M.J. **Invited Lecture**, Singapore International Chemical Conference, Singapore, December 2001 (cancelled because of 9/11 related issues).
69. Zaworotko, M.J. **Invited Keynote Lecture**, "Research Trends in Science and Technology 2002, Beirut and Byblos, Lebanon, March 2002.
70. Zaworotko, M.J. **Invited Lecture**, "Finite and Infinite Polygonal Assemblies", 223<sup>rd</sup> American Chemical Society National Meeting, Orlando, April 2002.
71. Zaworotko, M.J. **Invited Lecture**, "Binary Crystals by Design", 223rd American Chemical Society National Meeting, Orlando, April 2002.
72. Zaworotko, M.J. **Invited Lecture**, "Crystal Engineering with Pharmaceuticals: Design of the Composition and Structure of Pharmaceutical Phases", Higuchi Research Seminar, Kansas, May 2002.
73. Zaworotko, M.J. **Invited Lecture**, "Self-assembly of Crystals and Nanocrystals", American Crystallographic Association, San Antonio, May 2002.
74. Zaworotko, M.J. **Invited Lecture**, "Self-assembly of Crystals and Molecules with Nanoscale Features". 85th Canadian Society for Chemistry Conference, Vancouver, British Columbia, June 2002.
75. Zaworotko, M.J. **Invited Microsymposium Lecture**, 18<sup>th</sup> Congress and General Assembly of the International Union of Crystallography, Geneva, Switzerland, August 2002.
76. Zaworotko, M.J. **Invited Lecture**, SE Region ACS, Charleston, November 2002.
77. Zaworotko, M.J. **Invited Lecture**, "Crystal Engineering of the Composition of Pharmaceutical Phases", ACS Prospective on Polymorphism in Crystals, Tampa, February 2003.
78. Zaworotko, M.J. "Crystal Engineering of the Composition of Pharmaceutical Solids", 225<sup>th</sup> ACS National Meeting, New Orleans, March 2003.

79. Zaworotko, M.J.; Moulton, B.; Lu, J.; McManus, G.; Wong, R.; Rather, B. **Invited Lecture**, "Crystal Engineering of Coordination Compounds with Nanoscale Features", FAME 2003, Orlando, May 2003.
80. Zaworotko, M.J. **Invited Lecture**, "Crystal Engineering of the Composition of Pharmaceutical Phases", Strategies for Improving Solubility Workshop, Philadelphia, June 2003.
81. Zaworotko, M.J. **Invited Lecture**, "From Crystal Engineering of Coordination Polymers to Design of Nanoscale Molecules", 39<sup>th</sup> IUPAC Congress, Ottawa, Canada, August 2003.
82. Zaworotko, M.J. **Invited Lecture**, "Coordination Polymers with Nanoscale Features", 39<sup>th</sup> IUPAC Congress, Ottawa, Canada, August 2003.
83. Zaworotko, M.J. **Invited Lecture**, "Crystal Engineering of the Composition of Pharmaceutical Phases", 39<sup>th</sup> IUPAC Congress, Ottawa, Canada, August 2003.
84. Zaworotko, M.J. **Invited Lecture**. "Crystal Engineering of the Composition of Pharmaceutical Phases", Strategies for Improving Solubility Workshop, Brussels, Belgium Oct. 2003.
85. Zaworotko, M.J. **Invited Lecture**. "Self-Assembly of Nanoscale Chemical Structures", ICMAT, Singapore, Dec. 2003.

### Conference/symposium organizer

1. ACS Great Lakes Regional Meeting, DeKalb Illinois, 1990. A symposium on organometallics in synthesis.
2. Halifax CSC 1991: a symposium devoted to main group chemistry.
3. Halifax Atlantic CIC: conference titled "Synthetic Chemistry in Atlantic Canada"
4. Guelph CSC 1995: symposium titled "Back to the Future: A Symposium Celebrating 100 years of X-rays".
5. Newfoundland CSC 1996: symposium titled "Extended Metal Systems" (with C.R. Lucas).
6. Nova Scotia, NATO ASI 1996: two week summer school titled "Crystal Engineering: The Design and Application of Functional Solids" (with K.R. Seddon).
7. Cancun, 5<sup>th</sup> N. American Chemical Congress 1997. "Crystal Engineering" (with R.D. Rogers).
8. Washington DC American Crystallographic Association Meeting 1998, Transactions Symposium. "Crystal Engineering" (with R.D. Rogers).
9. Anaheim ACS Meeting 1999: inorganic division symposium "Transition metal coordination polymers" (with R.D. Rogers)
10. Glasgow IUCr, 1999: symposium devoted to crystal engineering (with R.D. Rogers, G.R. Desiraju)
11. Gordon Research Conference, 2000, "Organic Structures and Properties" (co-chair with M.D. Ward)
12. Pacifichem 2000, Hawaii, 2000, symposium devoted to applications of crystal engineering (with R.D. Rogers)
13. SERMACS 2002, Charleston, SC, "Crystals and Nanocrystals by Design" (with W.T. Pennington).

# From Molecules to Crystal Engineering: Supramolecular Isomerism and Polymorphism in Network Solids

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## I. Introduction

Whereas single-crystal X-ray crystallography has represented an active area of research since shortly after the discovery of X-rays, the subjects of crystal design and crystal engineering have developed rapidly only in recent years. This is presumably an



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Michael J. Zaworotko was born in South Wales, U.K., and received his B.Sc. degree from Imperial College, London, in 1977. He earned his Ph.D. degree in Chemistry in 1982 at the University of Alabama under the supervision of Professor Atwood in the field of organoaluminum chemistry. After completing a postdoctoral fellowship with Professor Stobart at the University of Victoria, Canada, he accepted an Assistant Professor position at Saint Mary's University (Halifax, Nova Scotia) in 1985. His research program initially focused upon organometallic chemistry and ionic liquids but soon evolved toward the solid state, in particular crystal engineering of organic and metal-organic networks. He became Professor and Chair of Chemistry at the University of South Florida in Tampa, FL, in 1999. artifact of a number of factors. For example, the development of relatively low-cost and powerful computers has not only enhanced crystal structure determination, but also crystal structure visualiza-

tion, database development and analysis, and reflection analysis and processing. Simply put, X-ray crystallographic analysis has become less time consuming, relatively inexpensive, and more readily available, even for larger and/or difficult structures. The growth of crystal engineering has also coincided with advances in our understanding of intermolecular interactions and supramolecular chemistry and the realization that several aspects of solid-state chemistry are of increasing relevance and can only be resolved with a better understanding of structure–function relationships. It is the latter that will be the primary focus of this review, which is to present an overview of how advances in supramolecular chemistry have impacted the manner in which chemists view the existence of single crystals and, perhaps even more importantly, the design of new crystalline phases.

## A. From Molecules to Crystal Engineering

*"One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition."* This provocative comment by Maddox<sup>1</sup> illuminates an issue that continues to represent a challenge of the highest level of scientific and technological importance. Simply put, to quote Feynman, "*What would the properties of materials be if we could really arrange the atoms the way we want them?*"<sup>2</sup> Such a dream generally remains to come to fruition, at least in terms of molecular self-assembly in the crystalline state. However, it has spawned and fuelled a seemingly exponential growth in research activity devoted to the subjects of crystal design and crystal engineering. Furthermore, the implications go beyond materials science since structure–function relationships in the solid state are of relevance to opportunities in the context of areas of interest that are as diverse as solvent-free synthesis and drug design and development. The term crystal engineering was first coined in a contribution by G. M. J. Schmidt concerning the subject of organic solid-state photochemistry.<sup>3</sup> Schmidt's article marked a thought evolution in at least two important ways. First, as implicit by use of the term crystal engineering, it became clear that, in appropriate circumstances, crystals could be thought of as the sum of a series of molecular recognition events, self-assembly, rather than the result of the need to "avoid a vacuum". It has subsequently become clear that crystal engineering, especially in the context of organic solids, is intimately linked to concepts that have been developed in supramolecular chemistry, another field that has undergone explosive growth in recent years. Supramolecular chemistry, defined by Lehn as chemistry beyond the molecule,<sup>4,5</sup> and "supramolecular assemblies" are inherently linked to the concepts of crystal engineering. In this context, crystals might be regarded as being single chemical entities and as such are perhaps the ultimate examples of supramolecular assemblies or supermolecules. Dunitz referred to organic crystals as "supermolecule(s) *par excellence*".<sup>6,7</sup> As revealed herein, this interpretation

is fully consistent with the approaches to crystal engineering practiced by ourselves and others who are presently active in the field.

Second, Schmidt's work emphasized that the physical and chemical properties of crystalline solids are as critically dependent upon the distribution of molecular components within the crystal lattice as the properties of its individual molecular components. Therefore, crystal engineering has implications that extend well beyond materials science and into areas as diverse as pharmaceutical development and synthetic chemistry. In the context of the former, there are important processes and intellectual property implications related to polymorphism.<sup>8–12</sup> In the context of the latter, solid-phase organic synthesis can be solvent free and offer significant yield and regioselectivity advantages over solution-phase reactions. In other words, crystals should not be regarded as chemical graveyards. To the contrary, it is becoming increasingly clear that binary or inclusion compounds can be used to effect a diverse range of thermal and photochemical reactions in the solid state,<sup>13–16</sup> including some that cannot be effected in solution.<sup>17–19</sup>

In this contribution we concentrate upon advances that were spawned by a series of papers and monographs in the 1980s by Desiraju<sup>20–22</sup> and Etter<sup>23–25</sup> that concentrated upon using the Cambridge Structural Database<sup>26</sup> (CSD) for analysis and interpretation of noncovalent bonding patterns in organic solids. It should be noted that a considerable body of work devoted to the subjects of crystal nucleation, growth, and morphology was developed concurrently. This research, which could be perhaps termed "engineering crystals", is not the intended focus of this review and is exemplified by the work of research groups such as those of Cohen,<sup>27</sup> Green,<sup>28</sup> Addadi,<sup>29–33</sup> Mann and Heywood,<sup>34,35</sup> Thomas,<sup>36,37</sup> and Davey.<sup>38,39</sup> The seminal work by Desiraju and Etter in solid-state organic chemistry afforded the concept of *supramolecular synthons*<sup>22</sup> and led to hydrogen bonds being perhaps the most widely exploited of the noncovalent interactions in the context of crystal engineering. Their research programs addressed the use of hydrogen bonding as a design element in crystal design and delineated the nature (strength and directionality) of the interaction. It is now readily accepted that these forces include weak hydrogen-bonding interactions such as C–H···X and CH···π. Although Professor Desiraju continues his valuable contributions to the discipline, Professor Etter passed away in 1992.

In this contribution, we attempt to address the challenges and opportunities represented by crystal engineering with particular emphasis upon how supramolecular concepts are important in helping us to understand supramolecular isomerism and superstructural diversity in the context of two classes of structure: coordination polymers and organic molecular networks.

## B. Crystal Engineering vs Crystal Structure Prediction

It is important to stress the significant conceptual difference between crystal engineering and crystal

structure prediction. In short, crystal structure prediction is precise (i.e., space group and exact details of packing are defined) and deals primarily with known molecules or compositions of molecules. Crystal engineering is less precise (e.g., network prediction) and most typically deals with entirely new phases, sometimes, but not necessarily, involving well-known molecules. Technological advances in experimental and computational methodology have accelerated the evolution of crystal engineering. In particular, the advent of CCD diffractometers facilitated the solution of crystal structures within hours or minutes rather than weeks or days and computational advances have made use of databases and visualization software inexpensive and straightforward. Therefore, although ab initio crystal structure prediction remains at best a significant challenge,<sup>40–43</sup> even for small molecules, crystal engineering has been able to develop rapidly because its objectives and *modus operandi* are distinctly different from crystal structure prediction. The *raison d'être* and strategies of crystal engineering are somewhat different from those of crystal structure prediction since the former is primarily concerned with design and, although more restrictive in terms of molecular components that might be employed, is becoming increasingly synonymous with the concept of supramolecular synthesis of new solid-state structures. In other words, crystal engineering represents a paradigm for synthesis of new solid phases with predictable stoichiometry and architecture. In contrast, predicting a crystal structure requires analysis of the recognition features of a molecular component in the context of how they will generate crystallographic symmetry operations and optimize close packing, i.e., it requires space group determination.

Engineering and design are far less restrictive from a conceptual perspective since they focus more broadly upon the design of new and existing architectures. In effect, the principles of design are based upon a blueprint, in many cases a blueprint that is first recognized via a serendipitous discovery, and allow the designer to select components in a judicious manner. Therefore, a desired network structure or blueprint can be limited to chemical moieties, in many cases commercially available moieties, that are predisposed to a successful outcome.

### C. Supramolecular Isomerism

Closely related to the well-documented (but not necessarily well understood) subject of polymorphism in crystalline solids is the existence of supramolecular isomerism<sup>44</sup> in polymeric network structures. Supramolecular isomerism in this context is the existence of more than one type of network superstructure for the same molecular building blocks and is therefore related to structural isomerism at the molecular level. In other words, the relationship between supramolecular isomerism and molecules is similar to that between molecules and atoms. In some instances, supramolecular isomerism can be a consequence of the effect of the same molecular components generating different supramolecular synthons and could be synonymous with polymorphism. How-

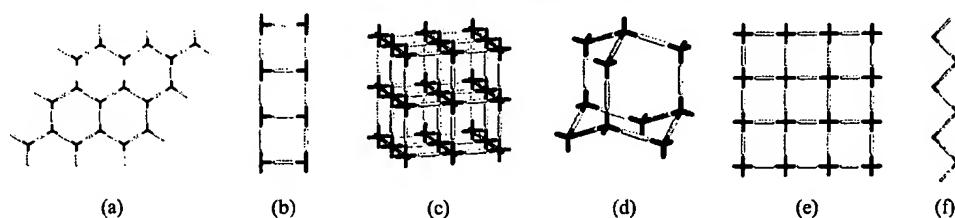
ever, in other situations, supramolecular isomerism is the existence of different architectures (i.e., architectural isomerism<sup>45</sup>) or superstructures. In this context, the presence of guest or solvent molecules that do not directly participate in the network itself, especially in open framework structures, is important to note as it means that polymorphism represents an inappropriate term to describe the superstructural differences between network structures. Indeed, it is reasonable to assert that polymorphism can be regarded as being a type of supramolecular isomerism but not necessarily vice versa. Pseudopolymorphism is a related term that has been coined to categorize solvates,<sup>46,47</sup> especially in the context of pharmaceutical solids. Since solvent molecules are often integral parts of the resulting network structures, a pseudopolymorph is, at least from a supramolecular perspective, a binary phase and an entirely different class of compound.

The subject of supramolecular isomerism is important for a number of reasons. (1) Investigation of the relationship between supramolecular isomerism and polymorphism represents a fundamental scientific challenge. However, when one considers that bulk properties of solids are critically dependent upon architecture and that crystal structure confirms composition of matter from a legal perspective, the applied relevance also becomes immediately apparent. Polymorphism in molecular crystals represents a phenomenon that is particularly important and ubiquitous in the context of pharmaceuticals and is receiving increasing attention from a scientific perspective.<sup>48–53</sup> It should also be noted that McCrone was prompted to suggest that the “*number of forms known for a given compound is proportional to the time and money spent in research on that compound*”.<sup>54</sup> However, the generality of McCrone's statement remains ambiguous despite indications that polymorphism is more general than expected from the CSD.<sup>55</sup> For example, Desiraju<sup>47</sup> demonstrated that the frequency of occurrence of polymorphic modifications is not necessarily uniform in all categories of substance. His analysis revealed that the phenomenon is probably more common with molecules that have conformational flexibility and/or multiple groups capable of hydrogen bonding or coordination. Coincidentally and importantly, this is inherently the situation for many pharmaceuticals and conformational polymorphism is a subject in its own right.<sup>56,57</sup> Desiraju also suggested that polymorphism can be strongly solvent-dependent. In summary, the relevance of polymorphism is clear but remains a subject that is not fully or widely understood at a fundamental level.

(2) Control over supramolecular isomers and polymorphs lies at the very heart of the concept of crystal engineering (i.e., design of solids). However, there is presently very little understanding concerning even the existence of supramolecular isomers, never mind how to control them.

(3) Supramolecular isomerism also lies at the heart of gaining a better understanding of supramolecular synthons and, by inference, how they develop and occur in other solid phases and even solution. The

**Scheme 1. Schematic Representation of Some of the Simple Network Architectures Structurally Characterized for Metal–Organic Polymers:** (a) 2D Honeycomb, (b) 1D Ladder, (c) 3D Octahedral, (d) 3D Hexagonal Diamondoid, (e) 2D Square Grid, and (f) 1D Zigzag Chain



Cambridge Structural Database remains a very powerful tool in this context, but it must be remembered that even such a large database will not necessarily be reflective of the full range of compounds that will be isolated and characterized in future years.

The conceptual link between polymorphism and supramolecular isomerism in organic and metal–organic networks is not immediately apparent. However, since polymorphs can be rationalized on the basis of supramolecular interactions, polymorphism can be regarded as a type of supramolecular isomerism. Implicitly, all sets of polymorphs can therefore be regarded as being supramolecular isomers of one another but the reverse is not necessarily the case. It should also be noted that solvates are almost always different compounds from a crystal engineering perspective. The only exception would be in the case of inclusion compounds where the host framework remains intact in the presence of different solvent molecules, i.e., the solvent serves the function of being a guest molecule. Supramolecular isomerism as seen in metal–organic and organic networks may be classified based upon analogies drawn with isomerism at the molecular level. Thus far it is appropriate to categorize the following classes of supramolecular isomerism.

**Structural.** The components of the network (i.e., the metal moiety and the ligands or exofunctional organic molecule) remain the same but a different superstructure exists.<sup>44</sup> In such a situation, the networks are effectively different compounds even though their empirical formula and chemical components are identical.

**Conformational.** Conformational changes in flexible ligands such as bis(4-pyridyl)ethane generate a different but often related network architecture.<sup>44</sup> Conformational polymorphism is a closely related subject.<sup>56,57</sup>

**Catenane.** The different manner and degrees in which networks interpenetrate or interweave can afford significant variations in overall structure and properties depending upon the molecular building blocks that are utilized.<sup>58</sup> Interpenetrated and non-interpenetrated structures are effectively different compounds because their bulk properties will be so different.

**Optical.** Networks can be inherently chiral and can therefore crystallize in chiral (enantiomorphic) space groups. Therefore, an analogy can be drawn with homochiral compounds. This type of supramolecular isomerism lies at the heart of an important issue: spontaneous resolution of chiral solids.<sup>59–65</sup>

The remainder of this contribution reviews the subject of supramolecular isomerism and how it leads to superstructural diversity in network solids. Emphasis is placed upon metal–organic or coordination polymers and organic solids, respectively. However, it should be noted that the subject matter is divided along these lines for convenience only since the basic concepts apply equally well to both classes of compound.

## II. Coordination Polymers

Coordination polymers exemplify how crystal engineering has become a paradigm for the design of new supramolecular structures. In this context, the work of Wells is exhaustive and seminal and can serve as a reference point. Wells was primarily concerned with the overall structure of solids, particularly inorganic compounds.<sup>66,67</sup> He defined crystal structures in terms of their topology by reducing them to a series of points (nodes) of a certain geometry (tetrahedral, trigonal planar, etc.) that are connected to a fixed number of other points. The resulting structures, which can also be calculated mathematically, can be either discrete (zero-dimensional) polyhedra or infinite (one-, two-, and three-dimensional) periodic nets.

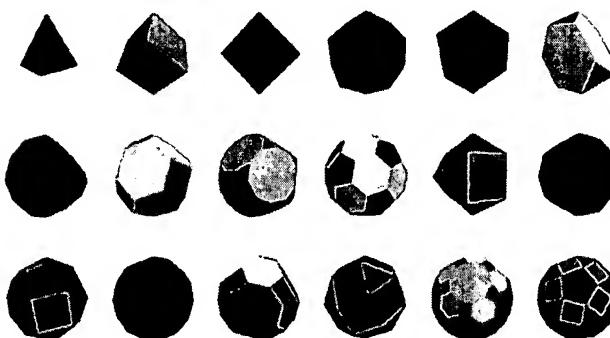
It is perhaps surprising that it took until the 1990s for the approach of Wells to bear fruit in the laboratory. Robson<sup>68–75</sup> was primarily responsible for the initial studies that facilitated rapid development of the field of coordination polymers alongside that of crystal engineering of organic solids. Robson extrapolated Wells work on inorganic network structures into the realm of metal–organic compounds and coordination polymers. In this context, the resulting “node and spacer” approach has been remarkably successful at producing predictable network architectures. Scheme 1 illustrates some of the simplest architectures that can be generated by using commonly available metal moieties and linking them with linear “spacer” ligands. Whereas diamondoid networks represent a class of structure that could be described as mineralomimetic because there are many naturally occurring analogues, that is not the case for any of the other architectures illustrated in Scheme 1.

The nature of these novel structures and their organic analogues and the diversity exhibited by their supramolecular isomers<sup>44</sup> represent the primary focus for the remainder of this contribution. Such structures are of interest for both conceptual reasons and because of their interesting properties. They are

ideally suited to illustrate the concepts of crystal engineering for the following reasons. (1) The diversity of structures that can be obtained from the simplest of components is quite remarkable, not only in the context of coordination polymers but also in the context of organic solids and even, for that matter, discrete architectures. (2) Coordination polymers can be relevant in the context of inclusion chemistry. As should be clear from Scheme 1, a recurring feature of even the simplest network structures is the presence of voids or cavities that are inherently present because of the architecture itself and the dimensions of the spacer ligands. This feature is attracting considerable interest, and there are a number of recent reports concerning open framework coordination polymers that exhibit hitherto unprecedented levels of porosity and high levels of thermal stability. Indeed, there already exists a diverse range of coordination polymers with higher effective surface areas than zeolites and stability to loss of guest.<sup>76–84</sup> (3) From a design perspective, it should be clear from Scheme 1 that each of the networks illustrated is based upon at least two components (i.e., the node and the spacer) and, as will become clear herein, such components can be preselected for their ability to self-assemble. The network structures can therefore be regarded as examples of blueprints for the construction of networks that, in principle, can be generated from a diverse range of chemical components, i.e., they are prototypal examples of modular frameworks. It should be noted that the construction of networks from single-component systems also represents an important area of activity. Self-assembly of a single-molecular component, or “molecular tectonics”, represents a different approach to crystal design, and it must be remembered that most existing crystal structures are based upon a single component. However, in order for single-component self-assembly to be directly relevant in the context of crystal engineering, all the molecular recognition features that lead to supramolecular synthons must be present in a single molecule. 1,3,5,7-Adamantanetetraacetic acid<sup>85,86</sup> and methanetetraacetic acid<sup>87</sup> can be regarded as being prototypal for self-assembled diamondoid architectures. Both structures are sustained by one of the most well recognized supramolecular synthons—the carboxylic acid dimer.<sup>88</sup> Pyridone dimers have been used in a fashion similar to build diamondoid networks, in this case from tetrahedral tetrakispyridones.<sup>89</sup> A number of well-known inorganic structures can also be regarded as examples of self-assembly (e.g., ice, potassium dihydrogenphosphate), and one might even consider covalent bonds as conceptually related: diamond, Si, Ge, ZnS, BP, GaAs, ZnSe, CdS, CuInSe<sub>2</sub>, CuFeS<sub>2</sub> (chalcopyrite). However, this contribution will focus primarily upon the modular or multicomponent approach to crystal design. Coordination polymers and hydrogen-bonded structures with multiple complementary components can be regarded as being the consequence of modular self-assembly.<sup>90</sup>

The remainder of this section will be organized according to the dimensionality of the observed

**Scheme 2. 3D Models of the Regular (Platonic) and Semiregular (Archimedean) Solids**



structures. However, it should be stressed that the modular self-assembly approach applies equally well to all levels of dimensionality since the dimensionality is often determined directly by the node. Therefore, it is appropriate to include discrete 0D structures in the discussion.

#### A. 0D (Discrete) Architectures

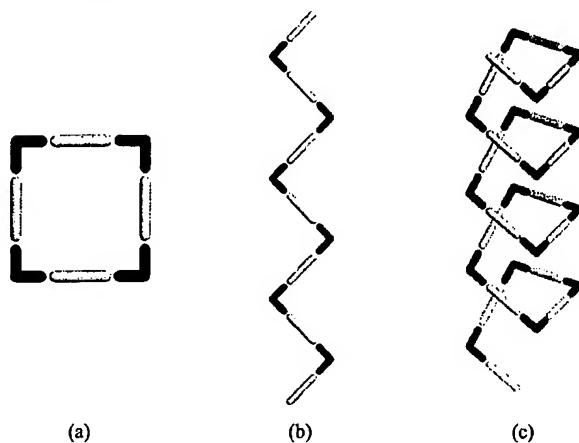
In addition to research that has focused upon infinite structures, the principles of self-assembly have also been applied toward the design and isolation of discrete molecular structures. Such structures are exemplified by molecular squares<sup>11,91–108</sup> and, more recently, by striking examples of new high molecular weight compounds that can be described as spheroid architectures.<sup>109–127</sup> The design principles behind the isolation and development of these new classes of compounds are based upon the concept of self-assembly in the context of geometric considerations found in regular (Platonic) and semiregular (Archimedean) solids. Such structures are also known in zeolites (e.g., Linde A, which is based upon an edge-skeleton generated by fused truncated octahedra<sup>128</sup>) and in biological self-assembled systems such as mammalian picornaoviruses<sup>93,99,129–131</sup> and proteins.<sup>132</sup> The 5 Platonic and 13 Archimedean solids<sup>133</sup> are illustrated in Scheme 2. They can be constructed at the molecular level by sharing of the edges of molecular moieties that have the shape of regular polygons,<sup>118</sup> i.e., triangles, squares, pentagons, hexagons, and octagons, or by connecting molecular vertices with linear bifunctional rodlike ligands.<sup>100,112</sup> In the case of the former closed convex surfaces are generated, whereas for the latter all the faces are open windows. This subject is highly topical, and several recent review articles have appeared.<sup>100,112,114,117,134</sup> We shall therefore provide no further details. The primary purpose of highlighting such structures is that they have been developed using the same principles as those used for generating the infinite structures described herein. Structures such as molecular squares are in effect supramolecular isomers of some of the infinite 1D structures described herein.

#### B. 1D Coordination Polymers

##### 1. Stoichiometry of Metal to Ligand = 1:1

Structural supramolecular isomerism is exemplified by the range of structures that has thus far been

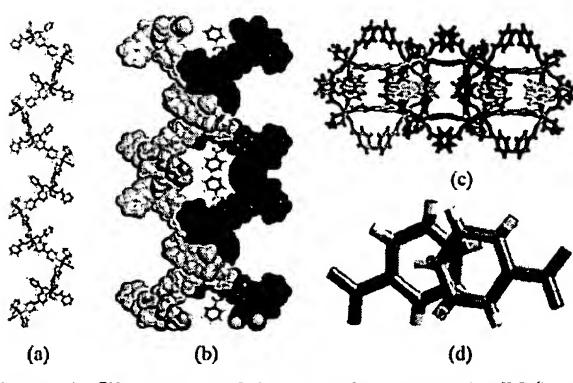
**Scheme 3. Schematic Representation of the Three Structural Supramolecular Isomers Observed for Angular Nodes Generated by *cis*-Substituted Metal Moieties: (a) 0D Square, (b) 1D Zigzag Chain, and (c) 1D Helix**



observed in coordination polymers, in particular network structures that have been observed for some of the simplest building blocks and stoichiometries. Scheme 3 illustrates the possible structures that can result from self-assembly of either a *cis*-octahedral or a *cis*-square planar metal and a linear "spacer" ligand. There are three obvious architectures that might result, and they are dramatically different from one another. The "square box" or "molecular square" architecture represents a discrete species that has been developed extensively in recent years by the groups of Fujita,<sup>106</sup> Stang,<sup>11,100,102–104,107,112,120</sup> and Hupp.<sup>92,94–96,98,101,135</sup> The other two architectures are both examples of 1D coordination polymers, but they are quite different from one another. The zigzag polymer<sup>136–146</sup> has been fairly widely encountered, and such structures tend to pack efficiently and eschew open frameworks or cavities. The helix<sup>147–158</sup> remains quite rare in the context of coordination polymers, but there is added interest because it is inherently chiral regardless of what its components might be. The inherent chirality of this architecture comes from spatial disposition rather than the presence of chiral atoms, thereby illustrating an important aspect of the solid state: it is possible for achiral molecules to generate chiral crystals. To illustrate the potential for generation of chiral architectures from simple achiral building blocks, let us consider how one might design a homochiral crystal from simple molecular components.

There would appear to be at least four strategies for the design of polar crystals that are independent of the need for homochiral molecular components: (1) achiral building blocks that crystallize in a chiral space group, (2) achiral molecular building blocks to build a chiral framework, (3) achiral host framework built from achiral molecular components with chiral guest(s), and (4) achiral host framework built from achiral molecular components with achiral guest(s).

Whereas exploitation of homochiral components represents the most obvious approach because the absence of a crystallographic center of inversion is guaranteed, it in no way implies or affords any

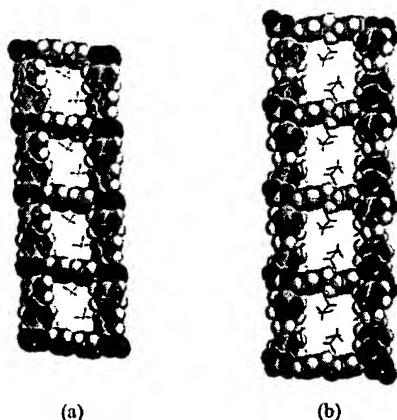


**Figure 1. Illustration of the crystal structure for  $[\text{Ni}(\text{bipy})(\text{PhCO}_2)_2(\text{MeOH})_2] \cdot \text{PhNO}_2$ :** (a) portion of a single helical chain, (b) space-filling model illustrating the packing of adjacent helices and the resulting cavities occupied by  $(\text{nitrobenzene})_2$  adducts, (c) overhead view of packing of helices, and (d) illustration of the dissymmetric nitrobenzene dimer.

control over molecular orientation and, therefore, bulk polarity. Furthermore, reliance upon the use of pure enantiomers raises the substantial problem of requiring control over stereochemistry at the molecular level without yet solving the problem of controlling stereochemistry at the supramolecular level. Indeed, strategy 1, which basically relies upon serendipity, offers just as much chance of optimal control of crystal packing as the use of homochiral components. However, there are three types of polar architecture that do not need to be sustained by homochiral molecular components: helical networks,<sup>149,153,154,159–166</sup> 1D acentric networks sustained by head-to-tail stacking of complementary molecules,<sup>167–175</sup> and host–guest networks which are polar because of the presence of acentric guest molecules or guest aggregates.<sup>65,176,177</sup>

Although the crystallization process for strategies 1–4 can inherently afford homochiral single crystals, only the use of homochiral components guarantees that all crystals in a batch will be of the same enantiomorph. Batches of crystals will often be heterochiral as both enantiomers tend to be formed equally during crystallization. Fortunately, it has been demonstrated that formation of homochiral bulk materials can be afforded by seeding with the desired enantiomer.<sup>153</sup>

$[\text{Ni}(\text{bipy})(\text{benzoate})_2(\text{MeOH})_2]$ <sup>154</sup> (bipy = 4,4'-bipyridine), **1**, illustrates the issues raised above. **1** self-assembles as a helical architecture that is sustained by linking of octahedral metal moieties with linear spacer ligands. Furthermore, it persists in the presence of several guests, even if 4-hydroxybenzoate ligands (i.e., ligands that are capable of forming strong hydrogen bonds) are employed. The crystal structure of the nitrobenzene clathrate is presented in Figure 1 and reveals the presence of large chiral cavities that induce the guest molecules to form chiral dimers. The guest molecules are trapped in a closed environment since helices from adjacent planes close off the  $500 \text{ \AA}^3$  cavities. The helical chains generated by **1** pack such that they are staggered but align in a parallel fashion. Therefore, the bulk crystal is polar as every helix in an individual crystal is of the same handedness.



**Figure 2.** Illustration of the crystal structures two molecule ladders: (a)  $[\text{Co}(\text{bipy})_{1.5}(\text{NO}_3)_2] \cdot 2\text{CHCl}_3$  and (b)  $[\text{Co}(\text{bipy-}\eta)_{1.5}(\text{NO}_3)_2] \cdot 3\text{CHCl}_3$ .

1 illustrates the attractiveness of self-assembly and crystal engineering for generation of polar architectures. In particular, there is no prerequisite for homochiral molecular components and host–guest compounds have the potential to be modular and fine-tunable since the guest molecule might be used to impart functional properties. It should also be stressed that, at least in principle, all existing achiral moieties can be incorporated into polar structures. The problem that has yet to be solved is how reliably and predictably to avoid crystallographic centers of inversion and how to control alignment of molecular dipoles.

Another example of a coordination polymer that self-assembles into a helical architecture is represented by the result of complexation of a 2,2'-bipyridine-based exo-ditopic macrocyclic ligand with  $\text{Ag}^+$  cations. The single-strand helical assembly is one of four possible arrangements and contains channels that run through the center of the assembly. These channels contain acetonitrile solvent molecules. The helices align antiparallel with respect to each other, and therefore, a racemic mixture of the right- and left-handed helices is obtained.<sup>155</sup>

## 2. Stoichiometry of Metal and Spacer Ligand = 1:1.5

Molecular ladders represent another type of 1D coordination polymer.<sup>59,91,178–185</sup> They differ in two important ways from molecular chains and helices. Most obviously, their stoichiometry is different since they are the result of self-assembly of 1.5 spacer ligands per metal. Therefore, the molecular building unit is effectively a “T-shape” moiety. Second, they necessarily contain cavities within the individual molecular ladders. These cavities are determined by the length, shape, and orientation of the spacer ligand. Simple examples of molecular ladders are represented by the coordination polymers  $[\text{M}(\mu-\text{L})_{1.5}(\text{NO}_3)_2]_n$  ( $\text{L}$  = bipy,<sup>186</sup> 2a, or bis(4-pyridyl)ethane),<sup>44</sup> 2b). Examples of these structures are illustrated in Figure 2, which reveals how 2a and 2b contain cavities that are large enough to sustain individual or pairs of molecules. The cavities are hydrophobic in nature, and their diagonal dimensions are defined by M–M separations of ca. 16 and 19 Å, respectively.

This means that the effective dimensions of the cavities are ca. 13 and 16 Å, respectively.

## C. 2D Coordination Polymers

The strategy of exploiting known coordination geometries of metals to propagate 2D structures via coordination with linear bifunctional spacer ligands has yielded many examples of coordination polymers with various metal moieties and architectures. The ratio of metal and ligand and the nature of the coordination of terminal ligands (i.e., degree of chelation) are the primary factors that determine the topology of the network. Scheme 4 illustrates some of the 2D network structures that have thus far been observed in coordination polymers.

### 1. Square Grids

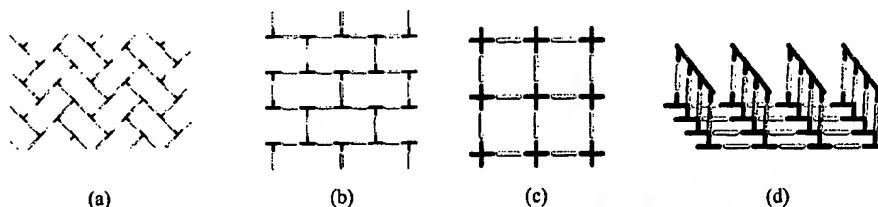
Square grid networks exemplify a particularly simple and commonly reported example of a predictable 2D metal–organic network. Square grid coordination polymers are based upon 1:2 metal:ligand complexes with linear bifunctional spacer ligands. They were first reported using cyano ligands<sup>187–190</sup> and have recently been expanded in terms of chemical type and cavity size to include pyrazines,<sup>191–193</sup> bipy,<sup>78,194–199</sup> and longer analogues of bipy.<sup>197,200</sup> These compounds can be regarded as being analogues of clays since they would be expected to have the ability to intercalate guest molecules. However, they have added features that are not likely to be present in clays. For example, cavities lie within the plane of the structure. These cavities are suitable for either interpenetration or entrapment of a possibly wide range of organic guest molecules. There also exists potential for incorporating catalytically active sites into such structures.<sup>70</sup> Furthermore, the cavities are tunable as the length and width of the spacer ligand controls the size of the cavities that occur within the polymeric structure, although interpenetration can mitigate against the existence of frameworks with very large cavities.<sup>58</sup>

Open framework square grid networks generated with bipy spacer ligands were first reported by Fujita et al.<sup>70</sup> Fujita's structures are based on Cd(II), and other examples have subsequently been reported based on a number of other transition metals, including Co(II), Ni(II), and Zn(II). Although these 2D coordination networks are isostructural within the coordination grid (effective dimensions of the diagonals are ca. 13 × 13 Å), the crystal structures of compounds can differ in the manner in which the networks stack with respect to each other (interlayer separations range from 6 to 8 Å).

The compounds  $[\text{M}(\text{bipy})_2(\text{NO}_3)_2]\cdot\text{guest}$  ( $\text{M} = \text{Co}, \text{Ni}$ ) have been studied extensively<sup>201</sup> by us, and we have only observed three basic crystal structure types (Figure 3).

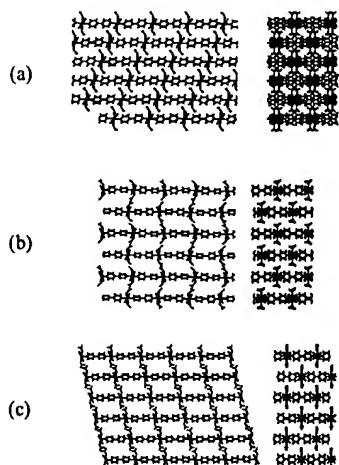
Type A compounds crystallize with similar cell parameters (monoclinic  $C2/c$ ,  $a = 21.5$  Å,  $b = 11.5$  Å,  $c = 13$  Å;  $\beta = 102^\circ$ ), have 2:1 guest:host stoichiometry and interplanar separations of ca. 6 Å. The crystal packing appears to be influenced by C–H···O hydrogen-bond interactions between the bipy ligands of one square grid and the nitrate anions of adjacent square

**Scheme 4.** Schematic Representation of 2D Networks Recently Reported for Metal–Organic Polymers: (a) Herringbone or ‘Parquet Floor’, (b) Brick Wall, (c) Square Grid, and (d) Bilayer

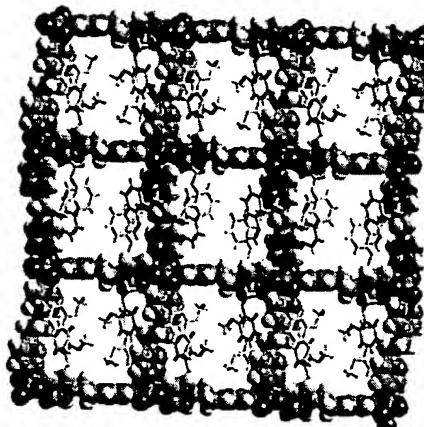


grids. The square grids do not align with a unit cell face, and adjacent grids are slipped in one direction by ca. 20%, i.e., every sixth layer repeats. The crystal packing of type B compounds is also controlled by weak interactions between adjacent layers. They generally crystallize with 2.5 guest molecules per metal center, and cell parameters are fairly consistent (monoclinic  $P2_1/c$ ;  $a = 16 \text{ \AA}$ ,  $b = 14.75 \text{ \AA}$ ,  $c = 16 \text{ \AA}$ ;  $\beta = 100^\circ$ ). The interlayer separation is ca. 8  $\text{\AA}$ . Type C compounds have interlayer separations that are similar to those seen for type B compounds. Four examples of type C compounds have 3:1 stoichiometry: three crystallize in space group  $C2/c$  (monoclinic;  $a = 16 \text{ \AA}$ ,  $b = 11.5 \text{ \AA}$ ,  $c = 23 \text{ \AA}$ ;  $\beta = 100^\circ$ ), and the other crystallizes in space group  $Cc$ . The latter compound exhibits similar cell parameters except that there is a tripling of the  $a$ -axis and the cell volume. Another example of a type C grid crystallizes in space group  $Pn$  (monoclinic;  $a = 11.4 \text{ \AA}$ ,  $b = 22.8 \text{ \AA}$ ,  $c = 15.9 \text{ \AA}$ ;  $\beta = 93.3^\circ$ ). Although these cell parameters are inconsistent with the previous four structures, the packing of the grids is appropriate for type C grids. The positioning of the grids facilitates inclusion of one guest molecule in the center of each grid. The other guest molecules lie between the grids and engage in stacking interactions between the bipy ligands and themselves.

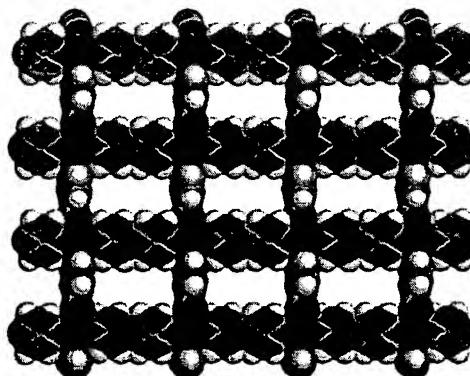
In all of these compounds the proportion of the crystal that is occupied by guest molecule is ca. 50 vol %. In such a situation it becomes reasonable to question whether interactions between the guest molecules determine the cavity shape and crystal packing of the square grid polymers rather than vice versa. This issue is addressed later.



**Figure 3.** Perspective views of the stacking of square grid network architectures of formula  $[M(\text{bipy})_2(\text{NO}_3)_2]$ : (a) A-type grids, (b) B-type grids, and (c) C-type grids.



**Figure 4.** Illustration of the square grid architecture  $[\text{Ni}(\text{bipy}-\eta)_2(\text{NO}_3)_2] \cdot 2\text{Ph}(\text{OMe})_2$ .



**Figure 5.** Space-filling illustration of  $[\text{Co}(\text{pyca})(\text{bipy})(\text{H}_2\text{O})_{1.5}] \cdot [\text{NO}_3] \cdot (\text{bipy})(\text{H}_2\text{O})_{1.5}$ ; an example of a rectangular grid resulting from the coordination of a metal to two types of spacer ligand.

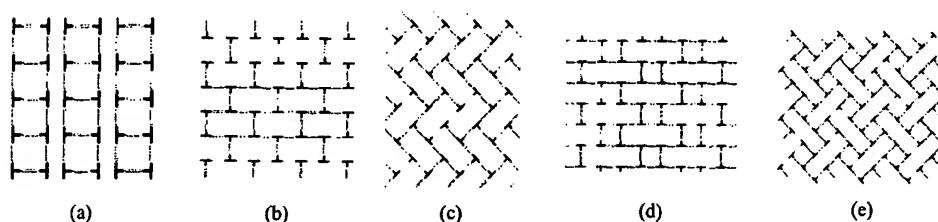
As these square grid architectures are inherently modular, it should be possible to extend their dimensions by simply using longer spacer ligands. An example of such a structure,  $[\text{Ni}(1,2\text{-bis}(4\text{-pyridyl})\text{-ethane})_2(\text{NO}_3)_2]_n \cdot 2\text{veratrole}$ , is illustrated in Figure 4. This structure has grid dimensions ca. 20% larger than the smaller grids (diagonal dimensions are ca.  $16 \times 16 \text{ \AA}$ ), large enough to enclathrate more than one aromatic guest. Larger grids (ca.  $20 \times 20 \text{ \AA}$ ) have also been reported using tetra(4-pyridyl)porphyrin.<sup>202</sup>

Grids in which there are two types of spacer ligand have also been reported.<sup>199,203</sup> Figure 5 reveals the structure of such a compound, which is appropriately termed a rectangular grid.

## 2. Other 2D Architectures

Another metal geometry or node that is of particular interest because of its potential range of su-

**Scheme 5. Schematic Illustration of Calculated Tiling Patterns Characterized or Might Be Expected To Occur: (a) 1D Ladder (finite second dimension), (b) Brick Wall, (c) Herringbone, (d) Long and Short Brick, (e) Basket Weave.** (d, e) Yet To Be Realized



Supramolecular isomers is the T-shaped geometry, i.e., a *mer*-substituted octahedral metal moiety or a trisubstituted square planar metal moiety with a 1:1.5 metal:spacer ligand ratio. This node has thus far produced examples of 1D, 2D, and 3D networks. Three distinct 2D supramolecular isomers have already been reported: brick wall,<sup>78,178,180,204–209</sup> herringbone,<sup>78,210–212</sup> and bilayer.<sup>213–216</sup> It is interesting to note that if one calculates the possible tiling patterns (i.e., all points lie in the same plane) that are possible for T-shaped nodes (Scheme 5), three of the five possibilities have already been realized.

The brick architecture (**5b**) is observed as the product of the reaction between heptacoordinate Cd(II) and 1,4-bis((4-pyridyl)methyl)-2,3,5,6-tetrafluorophenylene.<sup>70</sup> The T-shape geometry is the result of two terminal nitrate ligands chelating in a bidentate manner, thereby occupying four of the seven coordination sites. The structure is triply interpenetrated and, as such, does not possess channels or cavities. In a similar system using the nonfluorinated pyridyl-based ligand, a 1D ladder structure (**5a**) was observed. The brick architecture was also seen in [Ni(4,4'-azopyridine)<sub>1.5</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub>, which interpenetrates with two perpendicular [Ni(4,4'-azopyridine)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> square grid networks.<sup>208</sup>

The herringbone or 'parquet floor' architecture (**5c**) has recently been observed by several groups.<sup>204,210,211</sup> In these structures, the coordination sphere is similar to that of the brick architectures: heptacoordinate Cd(II) or Co(II) with two terminal bidentate nitrate ligands and coordination to one end of three 4,4'-azopyridine bridging ligands; an isostructural example has also been reported with 1,2-bis(4-pyridyl)-ethyne as the bridging ligand.<sup>214</sup>

The bilayer architecture has been observed in at least three compounds.<sup>213–215</sup> It has been observed as the product from the reaction of Co(NO<sub>3</sub>)<sub>2</sub> and bipy, which also generates ladder, square grid, and herringbone architectures. The bilayer form of [Co(bipy)<sub>1.5</sub>(NO<sub>3</sub>)<sub>2</sub>] is observed if crystallization occurs in the presence of CS<sub>2</sub> or H<sub>2</sub>O. The bilayers pack by partial interdigitation, which allows 1D channels to run through the structure. This structure is particularly relevant since it represents one of the first reported examples of a compound that might be termed a "metal–organic zeolite", i.e., the structure is porous and stable to loss of guest.<sup>215</sup> The bilayer architecture has also been reported for systems using 1,2-bis(4-pyridyl)ethane.<sup>217</sup>

The number of supramolecular isomers already observed in the Co(NO<sub>3</sub>)<sub>2</sub>/bipy system indicates how important selection of template and crystallization

conditions are. It seems reasonable to assert that it is only a matter of time and effort before the weave (**5e**) and long-and-short brick (**5d**) motifs illustrated in Scheme 5 will also be realized.

In terms of topology, it should be noted that brick and herringbone motifs are both examples of (6,3) nets and can therefore be regarded as being closely related to honeycomb (6,3) nets.<sup>67</sup> Honeycomb networks are quite common in organic structures because of the availability of trigonal nodes (i.e., 1,3,5-trisubstituted benzenes such as trimesic acid and species such as the guanidinium cation) but they seldom occur in the context of metal–organic polymers because trigonal and trigonal bipyramidal coordination geometries are rare. However, [Cu(pyrazine)<sub>1.5</sub>]BF<sub>4</sub><sup>218</sup> is based upon trigonal Cu(I), and it should therefore be unsurprising that it crystallizes as a honeycomb (6,3) net. That a number of ligands with trigonal geometry<sup>100,112,114,118,123,125,219–225</sup> now exist means that it is likely that a wider range of honeycomb structures will be generated soon.

## D. 3D Coordination Polymers

It might be anticipated that the challenge of designing 3D network architectures represents an added level of complexity in comparison with 2D architectures, and it in many ways represents the ultimate challenge to crystal engineers since it leads most directly to crystal structure control and prediction. For example, in most situations, a finite number of structural isomers can be calculated if all nodes must lie in the same plane. However, a larger number of possibilities might exist when that limitation is relaxed. It is therefore perhaps ironic that two of the simplest examples of predictable networks are exemplified by 3D networks generated via self-assembly of tetrahedral or octahedral nodes.

Tetrahedral nodes are predisposed to generate diamond-like (diamondoid) architectures, whereas octahedral nodes are expected to afford octahedral networks. These architectures can be obtained for both organic (typically hydrogen bonded) and metal–organic (i.e., coordination polymer) systems. Interpenetration can occur in these compounds, thereby mitigating against enclathration and porosity. However, interpenetration can also be exploited as a potentially important design paradigm for rational transformation of some of the 2D networks described earlier into 3D frameworks. This principle is discussed in a later section with respect to interpenetration of identical networks (homocatenation) and

interpenetration of different networks (heterocatenation).

## 1. Diamondoid Networks

The diversity of components that are available for crystal engineering of diamondoid networks and the means by which they self-assemble spans the full range of chemistry. The breadth of chemical moieties that might be used for crystal engineering is particularly well illustrated by the range of diamondoid networks that have been reported in recent years. Diamondoid architectures using a tetrahedral metal (Zn or Cd) as the node and cyanide ligands ( $\text{CN}^-$ ) as the spacer represent prototypal examples of diamondoid coordination polymers.  $\text{Zn}(\text{CN})_2$  and  $\text{Cd}(\text{CN})_2$  form diamondoid networks with 2-fold interpenetration.<sup>71,73–75</sup> However,  $\text{Cd}(\text{CN})_2$  can also be obtained as a single network with  $\text{CCl}_4$  filling the cavity.<sup>71</sup> This result illustrates two principles that have broad implications for crystal engineering: (1) Interpenetration can be avoided in the presence of an appropriate template or guest molecule; (2) Such compounds might be regarded as catenated and non-catenated supramolecular isomers of each other.

A diamondoid architecture also results when  $\text{Zn}(\text{CN})_4^{2-}$  is reacted with Cu(I). The resulting anionic network might be viewed as consisting of tetrahedral zinc nodes that are linked to tetrahedral copper nodes by cyanide spacers. However, the nature of coordination at the copper and zinc ions remains ambiguous. Analysis of the structural data indicated that it is most appropriate to consider the coordination of the copper as 100% organometallic (Cu–C) and the coordination of the zinc 100% metal–organic (Zn–N). The ionic nature of this particular framework means that the presence of a counterion in the resulting cavities is required.  $\text{N}(\text{CH}_3)_4^+$  fits comfortably inside the adamantoid cavity and precludes interpenetration.

A report<sup>226</sup> on the crystal structure and properties of  $[\text{Cu}(2,5\text{-dimethylpyrazine})_2(\text{PF}_6)]$  represents one of the first examples of a metal–organic diamondoid structure, and the related compound  $[\text{Cu}(4,4'\text{-bipy})_2](\text{PF}_6)$  was reported shortly thereafter.<sup>218</sup> Both structures exemplify the modular assembly design strategy and contain anions in the cavities generated by the diamondoid structure. In the case of the latter, the intermetallic separations are 11.16 Å and result in cavities that are sufficiently large to facilitate 4-fold interpenetration as well as inclusion of the counterions. A diamondoid architecture propagated by silver(I) and bipy,  $[\text{Ag}(4,4'\text{-bipy})_2](\text{CF}_3\text{SO}_3)$ , was reported<sup>227</sup> shortly thereafter, and it also exhibits 4-fold interpenetration with anions in cavities. The Ag–Ag separations are 11.6 Å. The 4-cyanopyridine analogue was reported in the same article and exhibits metal–metal separations of 9.93 Å. Despite the variations observed in the dimensions of these networks, both exhibit 4-fold levels of interpenetration.

Subsequent studies resulted in a plethora of diamondoid metal–organic structures and 2-, 3-, 4-, 5-, 7-, and 9-fold levels of interpenetration.<sup>228–231</sup> It should be noted that although interpenetration reduces or eliminates porosity, there are at least two

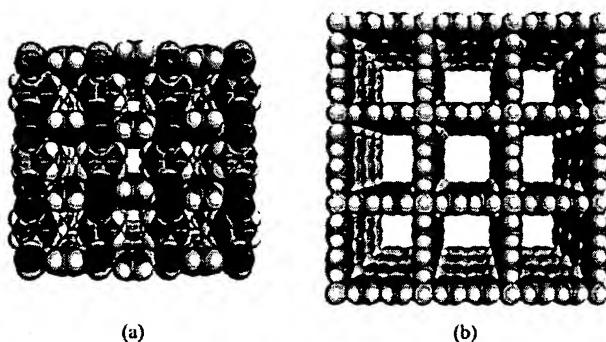
important properties that can be addressed with such structures. (1) They are predisposed to form acentric networks since there is no inherent center of inversion at a tetrahedral node. An odd level of interpenetration and an unsymmetrical ligand will definitely generate a structure that exhibits polarity.<sup>90</sup> (2) These structures could be useful for selective anion exchange.

In the context of the former, a series of neutral diamondoid architectures have been prepared with bridging ligands of varying size.<sup>74,218,228,231–233</sup> These compounds are of general formula  $\text{ML}_2$  ( $\text{M} = \text{T}_d$  metal; L = bridging anionic ligand), and it follows that a neutral network will be generated if a +2 metal is coordinated to two –1 anionic ligands.  $\text{Zn}(\text{isonicotinate})_2$  and  $\text{Cd}(\text{trans-4-pyridylacrylate})_2$  exhibit 3- and 5-fold degrees of interpenetration, respectively, and possess interesting properties in the context of polarity.<sup>228</sup> In the former compound, the Zn–Zn distance is ca. 8.8 Å. This is consistent with the previous structures that exhibit 4-fold interpenetration. The Cd–Cd distance is ca. 11.5 Å, similar to the intermetallic distances observed in the 4-fold interpenetrated structures that also contain counterions.

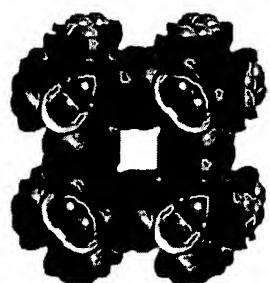
## 2. Octahedral Networks

Prototypal examples of octahedral networks are exemplified by iron cyano compounds. Such compounds are very well documented, and they have been used for centuries as pigments. An early X-ray study<sup>234</sup> of Berlin Green,  $[\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6]$ , Prussian Blue,  $[\text{KFe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6]$ , and Turnbull's Blue,  $[\text{K}_2\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6]$ , demonstrated that the iron cations act as the node in octahedral arrays in which they are linked by linear cyano ligands. These compounds form isostructural networks that vary only in the degree of potassium inclusion and the oxidation states of the iron atoms. Berlin Green can therefore be regarded as being the prototypal example of an open framework octahedral network; however, the limited length and lack of chemical versatility of the cyano ligand means that it has little relevance in the context of porosity.

Synthetic metal–organic octahedral networks were first reported in 1995.  $[\text{Ag}(\text{pyrazine})_3](\text{SbF}_6)$ <sup>235</sup> is sustained by octahedral Ag(I) cations and relatively short pyrazine ligands. The framework is necessarily cationic and is illustrated in Figure 6a. A neutral analogue is exemplified by  $[\text{Zn}(\text{bipy})_2(\text{SiF}_6)]$ .<sup>195</sup> In this structure (Figure 6b), the  $\text{SiF}_6^{2-}$  counterions cross-link the square grids that are formed by Zn and bipy to form a rigid octahedral polymer. The structure cannot interpenetrate because the walls of the channels are blocked by bipy ligands. The resulting channels have an effective cross-section 8 × 8 Å and represent ca. 50% of the volume of the crystal. Solvent molecules are readily eliminated but the framework collapses irreversibly upon loss of solvent. Perhaps the most salient feature of this structure is that the structure is entirely predictable in terms of both shape and dimensions.  $[\text{Zn}(\text{bipy})_2(\text{SiF}_6)]$  crystallizes in space group  $P4/mmm$  with  $Z = 1$ . In other words, the point group at Zn,  $D_{4h}$ , is propagated into



**Figure 6.** Space-filling models of two octahedral coordination polymers: (a)  $[\text{Ag}(\text{pyrazine})_3](\text{SbF}_6)$ ; (b)  $[\text{Zn}(4,4'\text{-bipyridine})_2(\text{SbF}_6)](\text{DMF})_x$ .



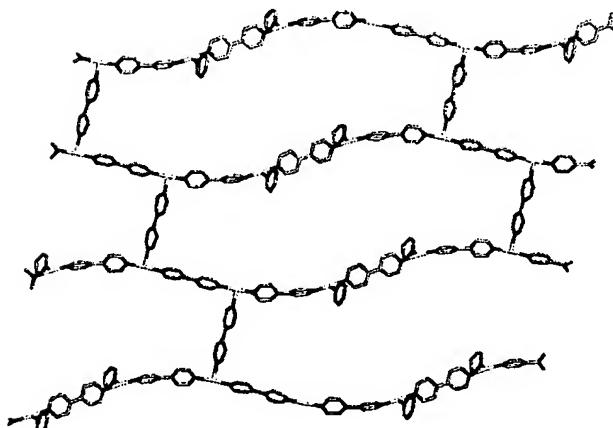
**Figure 7.** Space-filling illustration of  $\text{Zn}_4\text{O}(\text{BDC})_3$ : an octahedral coordination polymer generated from a tetrahedral node (SBU). The structure is octahedral because the six edges of the tetrahedral SBU are linked by spacer ligands. The area outside the shaded surface represents the accessible surface area, approximately 60% of the total cell volume.

space group symmetry. Furthermore, the cell parameters are determined by the intermetallic separations. The Cu analogue of  $[\text{Zn}(\text{bipy})_2(\text{SiF}_6)]$  is isostructural and is of particular relevance since it has a higher capacity for methane adsorption than any previously studied porous material and is stable to loss of guest.<sup>76</sup> Octahedral coordination polymers remain much less common than their diamondoid counterparts, but a recent report revealed a novel metal–organic coordination polymer,  $\text{Zn}_4\text{O}(\text{BDC})_3$  ( $\text{BDC} = 1,3\text{-benzenedicarboxylate}$ ), that suggests an exciting future for such compounds.<sup>81</sup>  $\text{Zn}_4\text{O}(\text{BDC})_3$  is a relatively simple and inexpensive material to prepare and is remarkably stable after loss or exchange of guest, remaining crystalline at temperatures above 300 °C. The key feature that makes  $\text{Zn}_4\text{O}(\text{BDC})_3$  special is that it exhibits a relative degree of porosity that is hitherto unprecedented in crystalline solids.

As revealed by Figure 7, the octahedral framework exhibits a large amount of surface area that remains accessible to guest molecules because it contains pores and cavities that are large enough to accommodate and release organic molecules such as chlorobenzene and dimethylformamide. Calculations and experimental data indicate that ca. 60% of the structure is available and accessible. This compares to the typical value of ca. 30% seen in zeolites.<sup>128</sup>

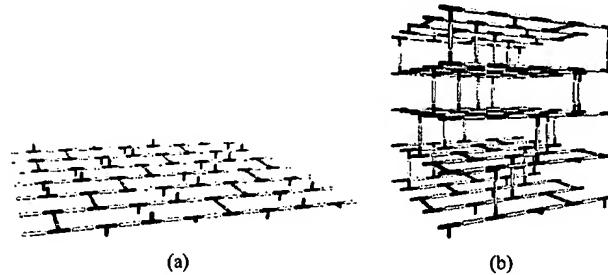
### 3. Other 3D Networks

In addition to the obvious, i.e., diamondoid and octahedral networks, there are numerous examples



**Figure 8.** Illustration of the cross-section of a single network of  $[\text{Co}(\text{bipy})_{1.5}(\text{NO}_3)_2] \cdot 1.5\text{benzene}$ ; effective dimensions of the cavity are ca.  $8 \times 40 \text{ \AA}$ .

**Scheme 6. Schematic Representation of the 3D-Frame Architecture: (a) Single Layer Illustrating the Large Cavities and the Relative Orientations of Adjacent T-Shaped Nodes and (b) Perspective View of the 3D Structure**



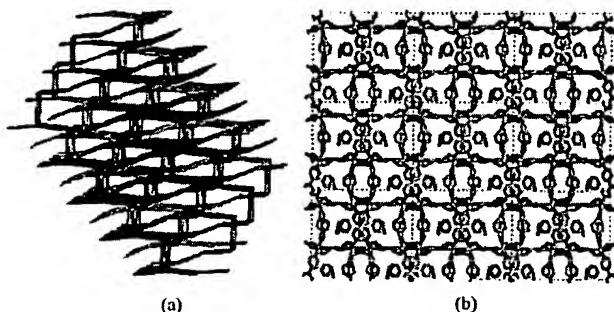
of novel 3D networks that have been observed in recent years. Many can be described as supramolecular isomers of low-dimensional structures. Two such structures are supramolecular isomers formed by self-assembly of T-shaped nodes. As discussed earlier, such self-assembly can afford 3D architectures that have not been seen in naturally occurring compounds. Scheme 6 reveals one of these structures:  $[\text{Co}(\text{bipy})_{1.5}(\text{NO}_3)_2] \cdot 1.5\text{benzene}$ .<sup>177</sup>

The cavities are revealed in Figure 8, and they are exceptionally large, having an effective cross-section of  $8 \times 40 \text{ \AA}$ . These large cavities are capable of sustaining both 3-fold interpenetration and inclusion of guest molecules in channels (Figure 9). Although the networks are inherently centrosymmetric, the crystal is polar because the guest molecules align in such a manner that their supramolecular structure cannot contain a center of inversion.

$[\text{Ag}(\text{bipy})(\text{NO}_3)]_n$  generates another type of supramolecular isomer for self-assembly of T-shaped components. It self-assembles into linear Ag–bipy chains that cross-link via Ag–Ag bonds. This particular 3D structure has been described as a “Lincoln Log”-type structure and exhibits a 3-fold level of interpenetration that is open enough to facilitate ion exchange of the loosely bound nitrate anions.<sup>236,237</sup>

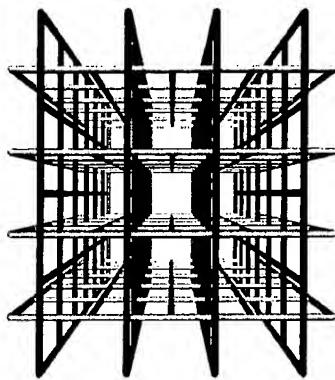
### 4. Hybrid Structures

An alternate approach to building 3D structures that seems to offer considerable potential is manipu-



**Figure 9.** Crystal structure of  $[\text{Co}(\text{bipy})_{1.5}(\text{NO}_3)_2] \cdot 1.5\text{-benzene}$ : (a) view illustrating the interpenetration of three networks and (b) illustration of the microchannels running parallel to the crystallographic z-axis. Polar 1D aggregates of benzene molecules are sustained by the channels.

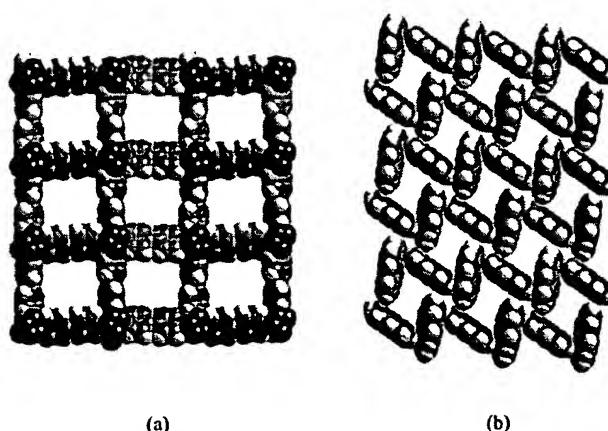
**Scheme 7. Schematic Illustrating How Porosity Can Be Generated by Inclined Interpenetration of Square Grid Networks**



lation of existing 2D structures. There are two relatively simple strategies in this context: cross-linking of 2D structures and interpenetration of identical or different 2D networks.

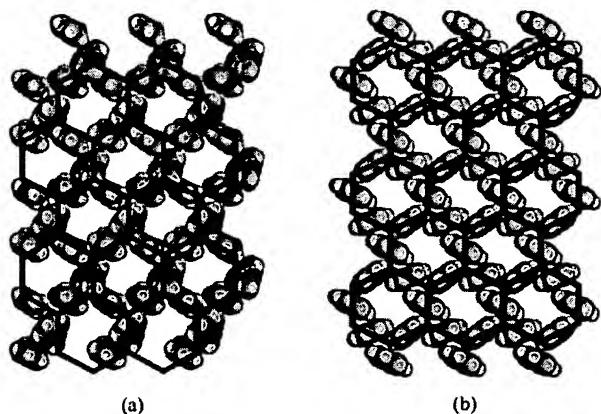
Cross-linking becomes feasible if one selects an appropriate 2D structure that has functionality in the axial direction. Such an approach has been widely used by clay chemists, and hence, the term "pillaring" might be applied to describe such a process.  $[\text{Zn}(\text{bipy})_2(\text{SiF}_6)]$  could be used as a prototype in the context of coordination polymers since it can be regarded as having been generated from square grid coordination polymers that are cross-linked by  $\mu\text{-SiF}_6$  anions. In the context of hydrogen-bonded structures, guanidinium sulfonates represent a class of compounds that have been cross-linked in a rational manner so as to generate infinite 3D structures.<sup>45,176,238-240</sup>

Interpenetration is a widely encountered phenomenon that mitigates against the existence of frameworks with very large cavities. However, Scheme 7 reveals that there are situations in which interpenetration can occur, generate porosity, and afford 3D structures. Square grid polymers that are based upon longer spacer ligands such as 1,2-bis(4-pyridyl)ethane (bipy-eta) or 1,2-bis(4-pyridyl)ethylene (bipy-ete) can interpenetrate in such a fashion.<sup>58</sup> However, an even more intriguing situation that could have important implications for design of new hybrid materials is exemplified by the crystal structure of the square grid coordination polymer  $\{[\text{Ni}(\text{bipy})_2(\text{NO}_3)_2] \cdot 2\text{pyrene}\}_n$ .<sup>241</sup>



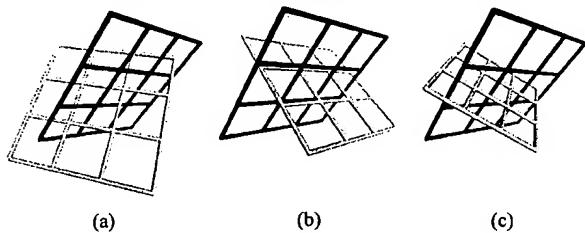
**Figure 10.** Space-filling illustrations of the two independent networks in  $[\text{Ni}(\text{bipy})_2(\text{NO}_3)_2] \cdot 2\text{C}_{10}\text{H}_8$ : (a) metal-organic coordination polymer square grid and (b) non-covalent aromatic (4,4)-net.

Careful examination of the crystal packing in this compound reveals that the pyrene molecules form an independent noncovalent network that is complementary from a topological perspective with the square grid. The resulting crystal represents a compound in which two very different types of 2D net interpenetrate. The square grid coordination networks (Figure 10a) possess inner cavities of ca.  $8 \times 8 \text{ \AA}$  and stack in such a manner that they lie parallel to one another with an interlayer separation of ca.  $7.9 \text{ \AA}$ . The pyrene nets (Figure 10b) are sustained by edge-to-face interactions and contain cavities of ca. dimensions  $6.5 \times 3.5 \text{ \AA}$ . The planes of the neighboring molecules intersect at an angle of ca.  $60^\circ$ , and there are no face-to-face stacking interactions between the molecules. The pyrene nets can be regarded as distorted (4,4) nets if the node is the point in space at which the vectors of the four pyrene planes intersect. An alternate interpretation is that nodes exist at the point of the edge-to-face interactions. The pyrene net could then be regarded as a distorted brick wall form of a (6,3) net. It is important to note that either a (4,4) or a (6,3) planar net is complementary from a topological sense with the (4,4) coordination polymer net and ensures that the coordination polymer nets must pack in a staggered manner. Given that cavity size within the pyrene nets is complementary with the width and height of a single aromatic ring, it should be unsurprising that the pyrene nets thread orthogonally with the bipy ligands of the coordination polymer via face-to-face and edge-to-face interactions and that the calculated volumes of the two nets are similar. This is to be expected based upon the observation that bipy square grids are self-complementary as they can interpenetrate in a 2-fold fashion.<sup>196</sup> The interpretation of this crystal structure as interpenetrating covalent and noncovalent nets is potentially important in the context of understanding the structure and stoichiometry of compounds that are based upon interpenetrated covalent and noncovalent nets. The structure also illustrates how polarity in crystals can be generated from subtle packing of achiral components, since the pyrene molecules form chiral nets.



**Figure 11.** Space-filling illustrations of two hexagonal (6,3)-networks formed by (a) naphthalene and (b) veratrole in the interpenetrated structures  $[\text{Ni}(\text{bipy})_2(\text{NO}_3)_2] \cdot \text{aromatic}$ .

**Scheme 8. Schematic Illustrating the Three Modes of Inclined Interpenetration Observed for Square Grid Networks: (a) Diagonal/Diagonal, (b) Parallel/Parallel, and (c) Parallel/Diagonal**



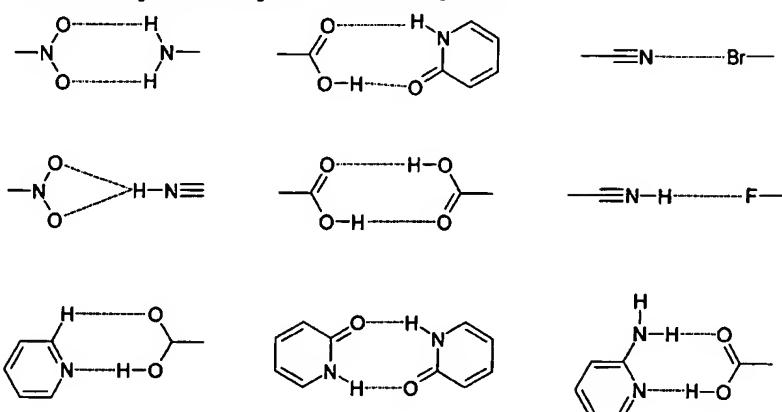
It should be noted that this type of packing is not found uniquely in  $\{[\text{Ni}(\text{bipy})_2(\text{NO}_3)_2] \cdot 2\text{pyrene}\}_n$ . Its naphthalene analogue,  $\{[\text{Ni}(\text{bipy})_2(\text{NO}_3)_2] \cdot 3\text{naphthalene}\}_n$ , can be interpreted as being the result of interpenetration of hexagonal and square nets,<sup>242</sup> and a study of a series of more than 20 related compounds has revealed the presence of noncovalent nets in every one of these compounds.<sup>243</sup> The noncovalent hexagonal nets formed by anisole and veratrole are illustrated in Figure 11.

That interpenetration can vary and be influenced by subtle effects are exemplified by this class of compound. It has been reported that for coordination polymers in which (4,4) networks that are planar and identical interpenetrate, two types of interpenetration are typically observed, both of which are examples of *inclined interpenetration*.<sup>58</sup> The most commonly encountered form might be described as *diagonal/diagonal inclined interpenetration*<sup>243</sup> and was observed in the prototypal  $[\text{M}(\text{bipy})_2\text{X}_2]_n$  compound,  $[\text{Zn}(\text{bipy})_2(\text{H}_2\text{O})_2]\text{SiF}_6$ .<sup>196</sup> The other mode of interpenetration might be described as *parallel/parallel inclined interpenetration*.<sup>208,244</sup> These types of interpenetration are illustrated in parts a and b of Scheme 8, respectively, and differ in how the networks orient and cut through each other. *Parallel* refers to the structure in which a "spacer" ligand from one network threads through the cavity of the other; *diagonal* refers to the structure in which a "node" from one network (e.g., the metal moiety) is within the cavity of the other. One would anticipate that the structure that is adapted by a particular compound would be influenced by several geometric factors: the

relative size of the cavity, the distance between adjacent nodes within a network, the thickness of the layers and how this limits the interlayer separation of adjacent networks, and the steric bulk of the node. In this context, it is important to note that with all other things equal, the diagonal/diagonal mode of interpenetration facilitates an interlayer separation that is 41.4% greater than that of the parallel/parallel mode. Furthermore, the diagonal/diagonal mode ensures a staggered orientation of parallel layers, whereas an eclipsed orientation is necessary if the parallel/parallel structure is present. Therefore, in terms of steric considerations, the diagonal/diagonal mode would appear most likely to be favored. However, circumstances where the interlayer separation would ideally be shorter or where the metal atoms in adjacent layers would be eclipsed (e.g., to maximize interlayer interactions) could favor the parallel/parallel mode.

The structures we have studied that are based upon complementary covalent and noncovalent networks exhibit a new mode of inclined interpenetration that is a hybrid of the modes described above: *parallel/diagonal inclined interpenetration*.<sup>243</sup> The noncovalent (4,4) arene networks exhibit parallel inclined interpenetration with respect to the (4,4) metal–organic coordination networks, whereas the covalent coordination networks demonstrate diagonal inclined interpenetration with respect to the arene networks (Scheme 8c). This salient structural feature means that the nitrate groups of adjacent parallel coordination polymer grids are staggered and that the interlayer separation is a consequence of the size of the arene network. It should therefore be unsurprising that type A grids result when templated by the smallest arenes (benzene and derivatives) as they exhibit smaller interlayer separations than types B and C packing. Grid types B and C occur in the presence of larger or more arenes.

Given that cavity size within the aromatic networks is complementary with the width and height of a single aromatic ring, the self-assembly of aromatic molecules in the compounds reported herein is readily sustained by edge-to-face and face-to-face interactions with the hydrocarbon portion of the bipy moieties. These interactions are presumably a primary driving force for the clathration of the guests and a mitigating factor against interpenetration. Interpenetration was not encountered in the square grid coordination polymer networks described above, and stacking interactions are seen in all compounds. It is also interesting to note that only three packing modes are observed in 13 compounds of similar composition. However, a question that cannot yet be answered with certainty concerns whether the noncovalent networks of aromatic molecules can exist in the absence of the coordination polymers. In this context, the existence of a 1:1 binary compound between ferrocene and pyrene<sup>245</sup> represents an important prototype since pairs of ferrocene molecules are stacked inside a pyrene 2D network that is sustained by noncovalent C–H···π interactions.

**Scheme 9. Representative Examples of Supramolecular Synths**

### III. Hydrogen-Bonded Networks

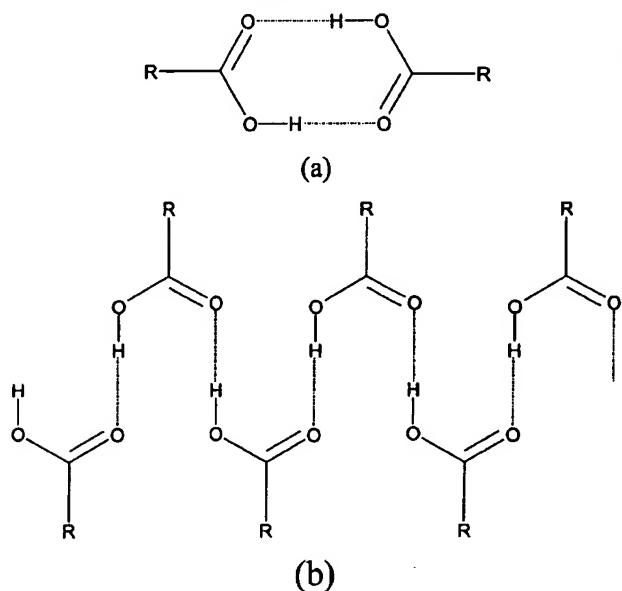
It would be inappropriate to attempt to present an exhaustive overview of crystal engineering of organic solids in this contribution. However, we feel that it is appropriate to highlight the analogies that can be drawn between hydrogen-bonded networks and coordination polymers. In particular, for hydrogen-bonded networks, the donor (i.e., a protic hydrogen atom) and the acceptor (i.e., a region of electron density) can be compared with metal atoms and ligands, respectively. Furthermore, as noted by Etter,<sup>25</sup> in cases where there are multiple hydrogen-bonding sites, there is a fair degree of predictability concerning which donors and acceptors will engage. Therefore, the "node and spacer" approach can be employed equally well with hydrogen bonds as with coordinate covalent bonds. Indeed, it is now realized that weak hydrogen bonds,<sup>246–251</sup> stacking interactions,<sup>20,252,253</sup> and halogen–halogen interactions<sup>254–256</sup> can also play a significant and predictable structure-determining role. However, we shall emphasize structures that are sustained by so-called strong hydrogen bonds, including ionic hydrogen bonds. For a more rigorous evaluation of the broader perspectives of hydrogen-bonded networks in the context of crystal engineering, one may consider looking at one of the many recent reviews on the subject.<sup>22,90,257–264</sup> In the context of this contribution, synthons that involve NH···O and/or OH···O hydrogen bonds, including those that exploit the carboxylic dimer or its deprotonated form, will be highlighted. They represent reliable and ubiquitous supramolecular synthons that already have been applied in a broad range of systems and have analogues in the context of coordination polymers.

It is only natural to analyze existing crystal structures by breaking them down, at least as far as is reasonably possible, into discrete aggregates or 1D, 2D, or 3D networks. At the very least, rationalization of crystal structures then becomes greatly simplified since even the presence of a reliable 1D network, for example, for a given set of molecular recognition features or supramolecular synthons significantly restricts the number of possible packing modes. An exciting byproduct of this thought process is that design of new compositions and crystal structures can also be achieved by thinking in terms of network

design. The concept of using this *supramolecular synthesis* approach to design new generations of infinite network structures offers enticing targets for both scientific and technological reasons. The greatest degree of predictability occurs if 2D and 3D architectures can be generated from first principles. In the case of the latter, the only degree of unpredictability would appear to relate to whether subtle conformational effects can affect structure or, in the case of open framework structures, as to whether interpenetration occurs. This approach to crystal engineering offers the intriguing concept of inherent control over the dimensions and molecular recognition features that are present in laminated or porous structures.

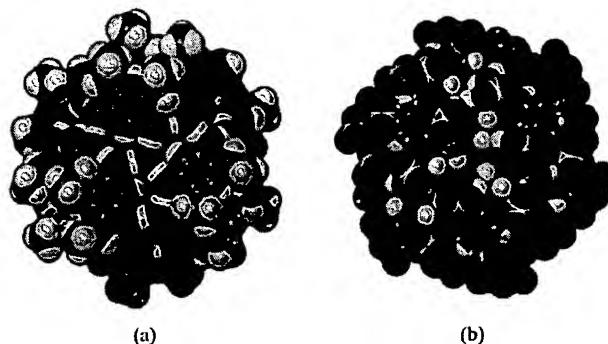
Scheme 9 illustrates some of the more common supramolecular synthons that have been exploited by crystal engineers to design and build organic molecular networks. The carboxylic acid moiety represents perhaps the most widely observed and exploited of these supramolecular synthons. This should be unsurprising since the carboxylic acid moiety is ubiquitous in organic chemistry. The carboxylic acid moiety also represents an ideal illustration of the problems associated with crystal structure prediction and design if one concentrates upon a molecular unit with a limited number of dimensions and molecular recognition sites. Monocarboxylic acids have been widely studied crystallographically, and it has been demonstrated<sup>88</sup> that there are two common motifs observed in the solid state for carboxylic acids. These supramolecular isomers, which profoundly influence the crystal packing and bulk properties, are illustrated in Scheme 10. As might be expected, the carboxylic dimer, A, is the most commonly observed supramolecular isomer and, being inherently centrosymmetric, tends to afford nonpolar crystals. However, since it is effectively a discrete 0D aggregate, there is little information that might be used in order to facilitate prediction of the overall crystal structure. The other motif, B, affords a 1D chain that is polar because it is the result of "head-to-tail" self-assembly. This simplifies to some extent the problem of crystal structure prediction, but it still does not address how these 1D chains pack. There is almost random choice of parallel or antiparallel packing of these chains in observed crystal struc-

**Scheme 10. Schematic Diagram Illustrating the Two Supramolecular Isomers for the Carboxylic Acid Supramolecular Synthon: (a) 0D Dimer and (b) 1D Head-to-Tail Chain**



tures. This is a subtle but important distinction since, in the case of parallel packing of chains, there is no crystallographic center of inversion within the 2D layer and crystallization in polar space groups therefore occurs in approximately 50% of structures that have thus far been characterized, i.e., centers of inversion between layers appear to occur in a random fashion. A similar situation occurs in the case of benzenedicarboxylic acids such as terephthalic acid. That terephthalic acid is inherently predisposed to form infinite 1D chains is intuitive. However, one must still jump from chains to grids to frames in order to generate a crystal structure. Indeed, terephthalic acid exhibits two polymorphs that are based upon identical chains that pack in different orientations.<sup>265,266</sup> It is possible to summarize the situation in the context of monocarboxylic acids and 1D structures as follows. (1) A lot of information can be generated by analyzing the crystal packing in monocarboxylic acids, including confirmation that the presence of a centrosymmetric supramolecular synthon (i.e., the carboxylic acid dimer) strongly tends toward centrosymmetric crystals. (2) Unfortunately, we still have only really learned what not to do if one wishes to design polar crystals (i.e., one should avoid a centrosymmetric supramolecular isomer) rather than what one must aim for in order to ensure optimized bulk polarity. (3) It appears that multiple molecular recognition sites will be necessary in order to gain a greater degree of predictability over organic crystal structures. Furthermore, the orientation of these recognition sites should be suitable for generation of at least a 2D network.

For the above reasons, our primary focus in the context of hydrogen-bonded networks will be 2D and 3D networks, prefaced by a brief discussion of discrete aggregates and 1D polymers.



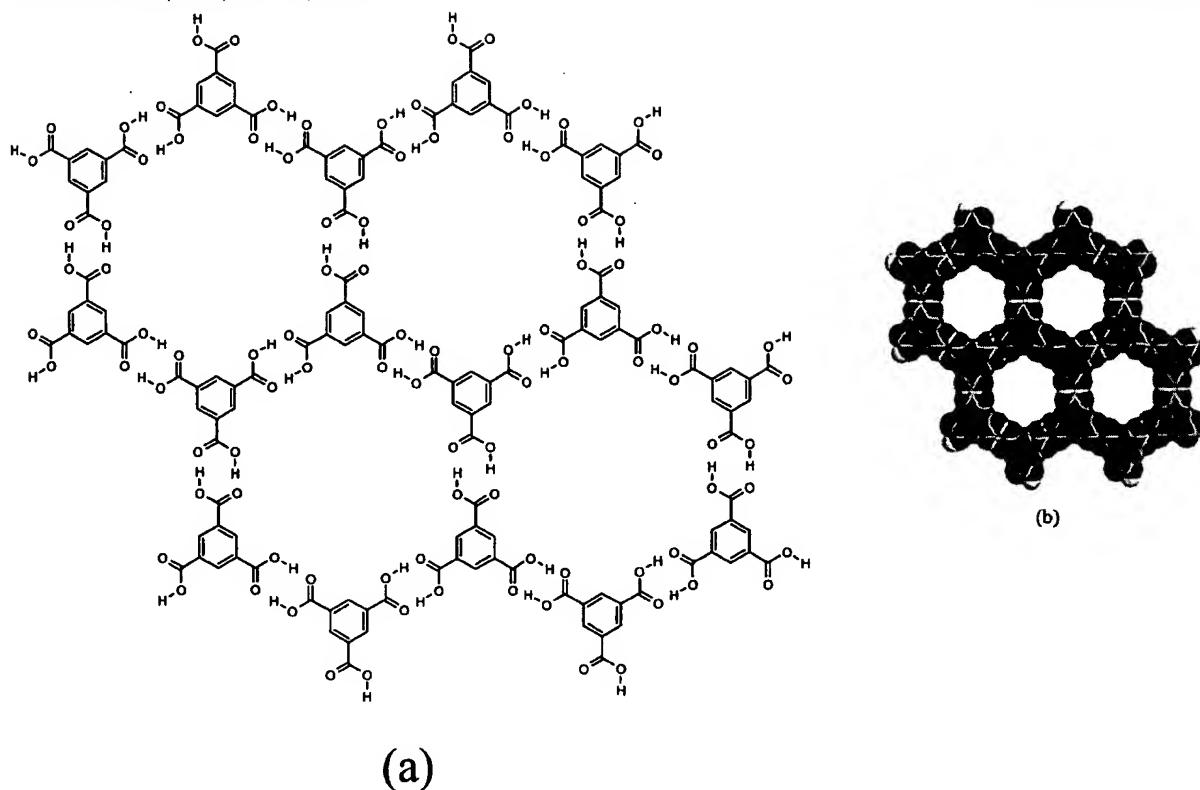
**Figure 12. Space-filling representations of large self-assembled spherical assemblies: (a) [*C*-methylresorcin[4]arene]<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub>, a snub cube, and (b) [(*p*-sulfonatocalix[4]arene)], a great rhombicuboctahedron.**

### A. 0D (Discrete) Aggregates and 1D Networks

The structures that can result from self-assembly of a *cis*-octahedral or a *cis*-square planar metal and a linear "spacer" ligand have been previously discussed in section II in the context of coordination polymers. The important geometric constraint introduced by the *cis*-conformation is the 90° vector imposed by the coordination geometry, i.e., it represents an angular node which can direct self-assembly into either a 1D zigzag, 1D helical, or 0D discrete cyclic motif. A prototypal example of an angular "node" in the context of hydrogen-bonded networks is isophthalic acid, which subtends a 120° angle between its carboxylic acid moieties. Although the preferred solid-state structure of isophthalic acid is the zigzag motif,<sup>267</sup> it has been demonstrated that self-assembly of a discrete hexameric aggregate that also persists in solution can be invoked by the addition of a bulky substituent to the 5-position on the benzene core.<sup>268,269</sup>

The exploitation of bulky substituents to direct the formation of discrete aggregates over infinite structures has also been shown to be successful in binary hydrogen-bonded systems, as exemplified by a series of 1:1 complexes formed from cyanuric acid and disubstituted melamines.<sup>270–275</sup> The relative bulkiness of the melamine substituents determines whether the structure adopts a linear tape (1D), crinkled tape (1D), or rosette (0D) structure, in order of increasing steric contribution.

A different strategy that has recently been employed for the isolation and development of discrete structures is based upon generating molecular polyhedra by using geometric considerations as found in Platonic and Archimedean solids. A prototypal example of such a structure<sup>121</sup> is the self-assembled *snub cube*<sup>276</sup> that occurs when calix-*C*-methylresorcin[4]arenes self-assemble with water molecules to form [*C*-methylresorcin[4]arene]<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub>. The resulting structure forms a spheroid held together by hydrogen bonds, and it possesses a very large enclosed cavity, 1375 Å<sup>3</sup>. A related structure<sup>116</sup> can be generated when *p*-sulfonatocalix[4]arenes self-assemble with pyridine-*N*-oxide, metal ions, and water. The resulting discrete structure is based upon a *rhombitruncated cuboctahedron*.<sup>277</sup> The two Archimedean structures are illustrated in Figure 12.



**Figure 13.** Honeycomb (6,3)-network observed for BTC (BTC = 1,3,5-benzenetricarboxylic acid): (a) schematic representation of the hydrogen-bonding pattern and (b) space-filling model illustrating the hexagonal channels that are formed.

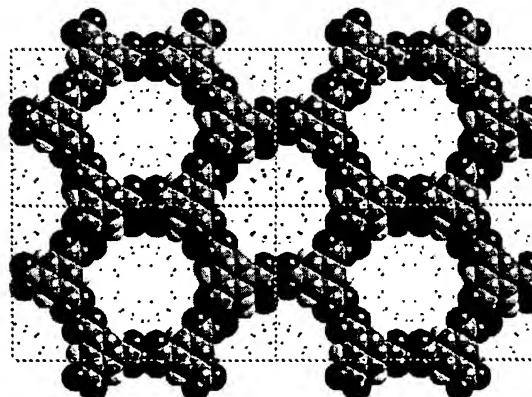
Many viruses have an outer shell, or capsid, that can be described as a hydrogen-bonded polyhedron (icosahedron).<sup>93</sup> The above synthetic structures may provide chemists with insight as to how to design nanoscale polyhedra for application in biological systems. In this context, it should also be noted that Etter reported a series of discrete binary adducts between acyclic imides and a series of cocrystallization aids.<sup>278</sup> This work also represents an attempt to better understand and ultimately control the type of hydrogen-bonding interactions that play such an important role in molecular recognition of biological systems.<sup>279</sup> It seems reasonable to assert that the studies of hydrogen-bonding patterns in the systems described above might indeed eventually aid in the design of structures that will impact biological systems.

## B. 2D Networks

Hydrogen-bonded 2D networks are exemplified by organic molecular networks that are constituted from organic moieties with multiple complementary terminal functional groups that necessarily assemble into 2D arrays because of their geometric disposition.

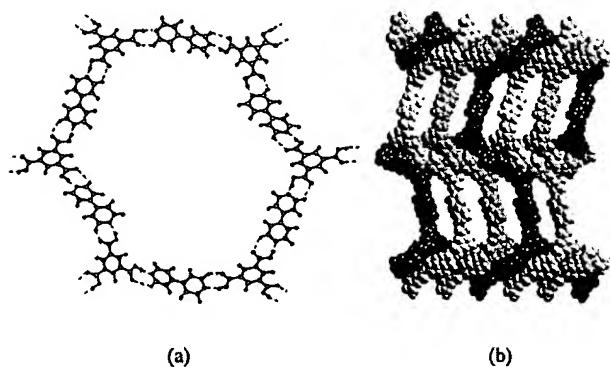
### 1. Derivatives of Trimesic Acid

The well-known structure of trimesic acid (1,3,5-benzene tricarboxylic acid, H<sub>3</sub>TMA), a polyfunctional carboxylic acid that is inexpensive and chemically robust, has long intrigued crystal engineers and represents a more suitable prototype for crystal structure prediction and design than mono- or dicarboxylic acids. It possesses trigonal exodentate func-



**Figure 14.** Space-filling illustration of the BTC·isooctane clathrate. The isooctane is disordered within the hexagonal channels.

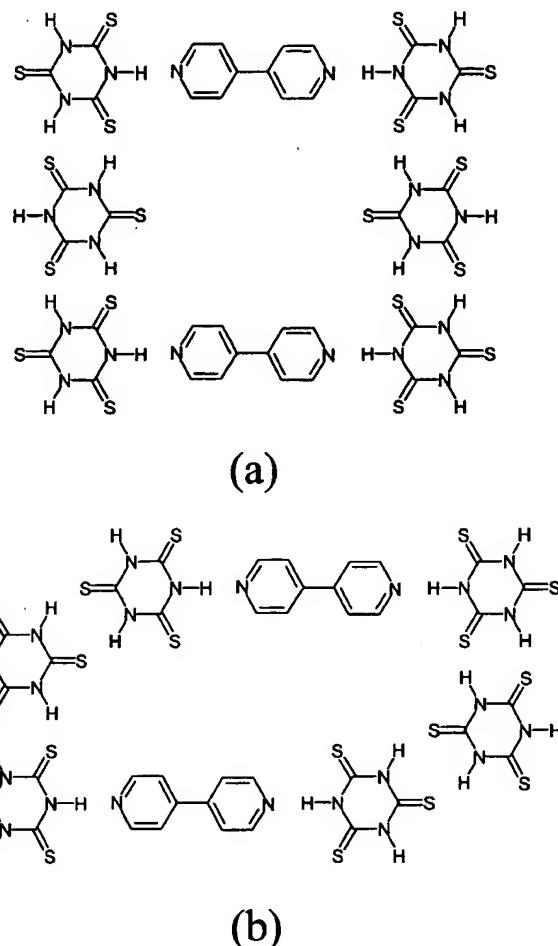
tionality that facilitates self-assembly into two dimensions. Figure 13 illustrates how the hydrogen-bonding pattern in the 2D networks formed by H<sub>3</sub>TMA generates cavities of predictable size (approximately 14 Å diameter). In pure H<sub>3</sub>TMA<sup>280</sup> the honeycomb grid is puckered and the cavities are filled by self-inclusion, or interpenetration, of other networks. However, subsequent reports revealed that there are methods for preparing a noninterpenetrated or open framework form of H<sub>3</sub>TMA.<sup>281,282</sup> If crystallized in the presence of alkanes, H<sub>3</sub>TMA forms open framework honeycomb layers that align in such a manner that adjacent sheets are almost eclipsed with respect to each other (Figure 14). The resulting architecture observed in the crystal structure is essentially identical to that depicted in Figure 13.

**Figure 15.**

$H_3TMA$  represents an example of a motif that is the result of the assembly of a single component that is self-complementary. As discussed earlier, this means that there are limits in terms of supramolecular synthesis when compared to multiple-component modular systems. The  $H_3TMA$  network can be extended to generate larger holes and, therefore, larger channels and cavities by employing the modular self-assembly approach. The structure of  $[H_3TMA][\text{bipy}]_{1.5}$  would be expected to exist as an expanded form of  $H_3TMA$  since the pyridine-carboxylic acid supramolecular synthon appears to be more stable than the carboxylic acid dimer itself.<sup>283–285</sup> As shown in Figure 15, the anticipated structure indeed occurs and the cavities are large (ca.  $26 \times 35 \text{ \AA}$ ). However, these cavities are filled by the interpenetration of three independent networks (Figure 15b), thereby affording a close-packed structure with no cavities. This type of interpenetration, which can be termed parallel interpenetration,<sup>10</sup> resembles weaving and is facilitated by puckering of the pseudohexagons that form the network. The hexagons resemble the chair conformation of cyclohexane.

Rao et al. recently reported a related structure that is based upon modular self-assembly:<sup>286</sup> an organic network formed by trithiocyanuric acid (TCA) and bipy. Adjacent layers are aligned parallel to each other, but there is no interpenetration. The resulting open framework structure exhibits channels with an effective diameter of  $10 \text{ \AA}$ . An interesting feature of this compound is that the cavities in the layers, and therefore the resulting channels, can vary in size depending on the solvent of crystallization that is used to template the modular self-assembly process. (Scheme 11). It should be noted that the two architectures that have thus been observed are not simply distorted or stretched variants of one another, they have distinct hydrogen-bonding patterns. Another salient feature is that there are sulfur atoms accessible in the cavities which could promote selective sorption or could facilitate desired chemical reactivity in the context of green chemistry.<sup>287</sup>

Network structures based upon metalloporphyrins with multioxodentate functionality (e.g., tetracarboxylic acid derivatives) have also yielded 2D networks sustained by hydrogen bonding.<sup>288</sup> An interesting feature of these structures is that the presence of a metal ion in the porphyrin ring can afford cross-linking of 2D layers by bidentate spacer ligands, thereby affording a 3D architecture.<sup>288</sup> Such an

**Scheme 11. Schematic of the Two Supramolecular Isomers Reported for the Modular Self-assembly of TCA and bipy**

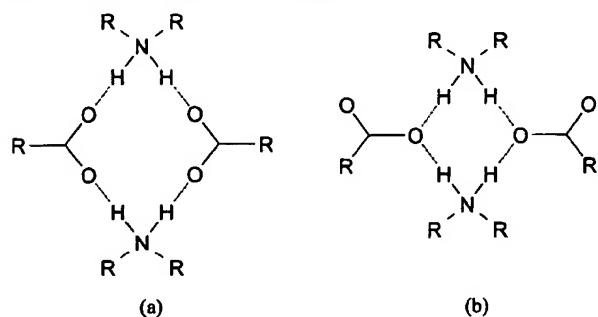
architecture is a hybrid form<sup>289</sup> of coordination polymer and organic network.

### 3. Hydrogen-Bonded Networks Sustained by Organic Ions

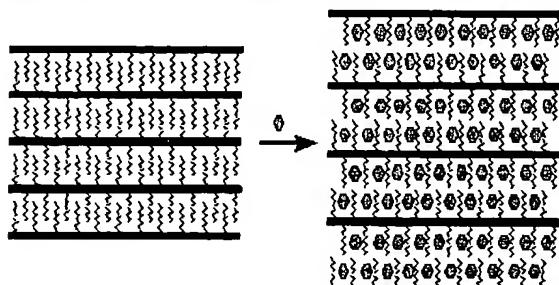
Salts that are based upon organic ions with complementary hydrogen-bonding sites represent an alternate approach to modular self-assembly of organic molecular components.  $H_3TMA$  also represents an appropriate precursor in this context, via formation of ammonium salts of the deprotonated forms of  $H_3TMA$ .<sup>290–292</sup> Although it might not at first be obvious how the ammonium moiety could extend anionic forms of  $H_3TMA$  into honeycomb networks, Scheme 12 illustrates two such motifs, the supramolecular isomers A and B, both of which facilitate linear propagation of carboxylate anions. In the case of  $TMA^{3-}$  and dicyclohexylammonium, supramolecular isomers A and B have both been observed to generate laminated structures. The generation of A or B appears to be solvent dependent. It has also been shown that self-assembly of the lamellar structure can occur at surfaces.<sup>293</sup>

An important feature of architectures that are sustained by A and B is that some of their components and features can be fine-tuned without destroying the basic architecture. For example, the

**Scheme 12. Schematic Illustration of Two Motifs that Can Occur through Self-assembly of Dialkylammonium and Carboxylate Moieties. Both Motifs Effect Linear Propagation**



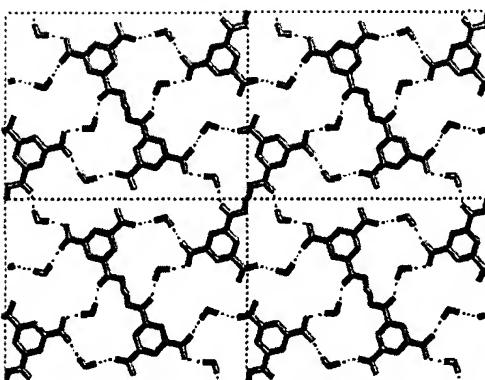
**Scheme 13. Schematic Illustration of the Interdigitation of the Alkyl Groups on Adjacent Layers in  $[(\text{BTC}^{2-})(\text{NH}_2(\text{alkyl})_2^+)_2]$  and the Possibility of Intercalation of Guest Molecules**



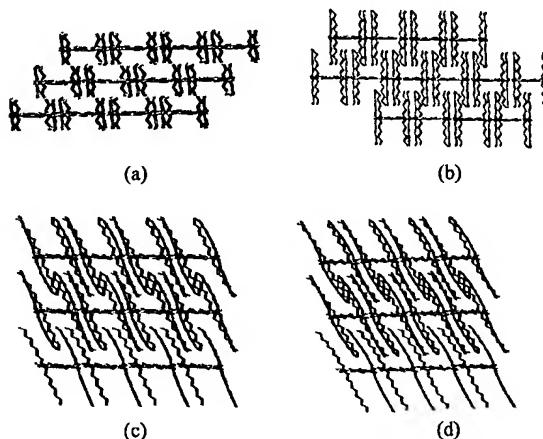
ammonium cation substituents can be changed without influencing the basic molecular recognition properties in the context of motifs A and B. For secondary amines, organic substituents would extend above and below the network and in appropriate circumstances would preclude interpenetration. Depending upon the nature of the substituents, adjacent layers might interdigitate and/or adopt clay-like intercalates in the presence of appropriate guest molecules (Scheme 13). Both HTMA<sup>2+</sup> and TMA<sup>3+</sup> can sustain laminar structures that result from crystallization of H<sub>3</sub>TMA in the presence of primary and secondary amines (RNH<sub>2</sub> and R<sub>2</sub>NH).

Related laminar architectures have also been synthesized using other polyfunctional carboxylic acids such as trimellitic and pyromellitic acids.<sup>294</sup> Stoichiometry has little influence over whether laminar structures are obtained, but it has a profound influence over the local hydrogen-bonding patterns and the molecular recognition features of the "organic clays" that are formed.

**Stoichiometry 1:2 ( $\text{H}_3\text{TMA}$ :amine).** The hydrogen-bond network within each sheet is hardly predictable, but it seems to be reproducible over a wide range of ammonium cations. The structure of the 2D network is illustrated in Figure 17, and it is composed entirely of ionic hydrogen bonds. If alkyl substituents are present on the ammonium cation, then the typical result is a laminated material with poor ability to adsorb molecules because of interdigitation of the alkyl substituents<sup>291</sup> (Figure 17). However, use of dibenzylamine (DBA),  $[(\text{PhCH}_2)_2\text{NH}]$ , mitigates against interdigitation and promotes re-

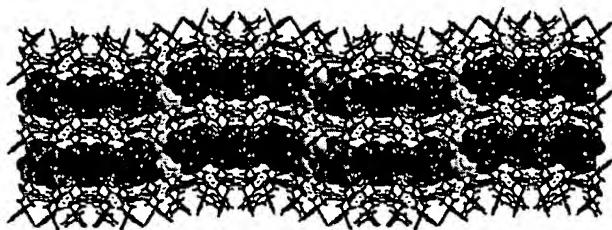


**Figure 16.** Illustration of the hydrogen-bonding pattern in  $\left[\text{BTC}^2-\right]_2\text{NH}_2(\text{CH}_2\text{Ph})_2\text{H}_2$ ; benzyl groups are omitted for clarity.

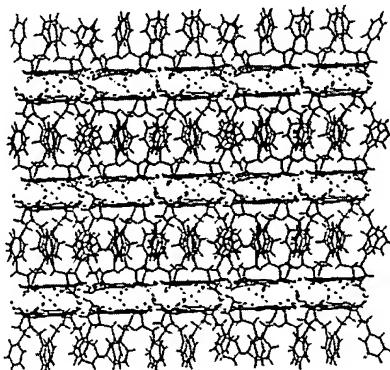


**Figure 17.** Illustrations of the packing interactions of the hydrogen-bonded 2D networks in  $[(\text{BTC}^{2-})(\text{NH}_2(\text{alkyl})_2^+)_2]$ , alkyl = (a) propyl, (b) hexyl, (c) octyl, and (d) decyl.

versible incorporation of aromatic guest molecules.<sup>290</sup> The resulting compounds are structurally related to clays, but they are inherently hydrophobic and have affinity for aromatic guests over alcohols or water. In this series of compounds, there is some variation in the geometry of the hydrogen-bond layer and in the manner in which guest molecules are incorporated. In general, the benzyl groups form a plethora of aromatic C–H $\cdots\pi$  interactions to the surrounding guest molecules. The unit cell lengths are typically multiples of ca.  $12 \times 17 \times 21$  Å (stacking axis, short axis, and long axis, respectively). The length of the stacking axis represents the interlayer separation, and a doubling of the length of the stacking axis occurs when adjacent layers are not related by translation. Multiples of short and long axes also occur because of differences in the arrangement of guest molecules between benzyl groups. In effect, guest molecules and/or benzyl groups do not necessarily repeat with the asymmetric unit of the H-bonded layer. The crystal structures might be classified based upon the stacking axis as being of one of two types: (a) identical packing of adjacent layers (i.e., related by translation) or (b) adjacent layers which are different from each other. The hydrogen-bonded sheets can be either flat or corrugated. In effect, the host matrix is a flexible, generic host material for aromatic molecules. A representative



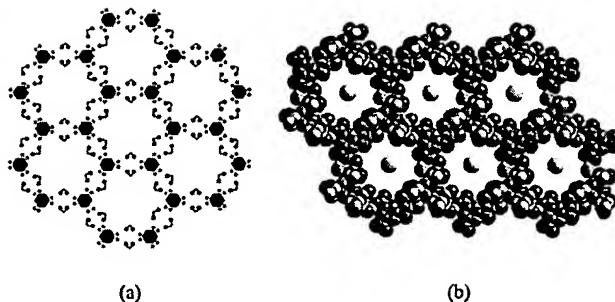
**Figure 18.** Illustration of the crystal packing of the hydrogen-bonded 2D networks in  $[(\text{BTC}^{2-})(\text{NH}_2(\text{CH}_2\text{Ph})_2^+)_2]$ . The benzyl moieties preclude interdigitation and facilitate reversible sorption of aromatic molecules.



**Figure 19.** Illustration of the crystal packing in  $[(\text{BTC}^{2-})(\text{NH}_3(\text{CH}_2\text{Ph})^+)_2]$ , a prototypal example of the network structures formed by BTC dianions and primary ammonium cations.

structure is illustrated in Figure 18, and as should be clear, there is no interdigitation of benzyl groups. The guest molecules interact with walls of the channels only, and the asymmetric unit is unusual: 3:3:1 for host:guest:solvent. In the presence of primary ammonium cations, similar structures are obtained but they are more appropriately termed bilayer architectures since there are alternating hydrophobic and hydrophilic regions. A typical structure is illustrated in Figure 19. Similar structures are obtained for both alkyl- and benzylammonium cations. It might be reasonable to describe such structures as being cytomimetic since there is a resemblance to the type of supramolecular synthons that exist in phospholipid membranes and in the solid phases of surfactants. The ancillary organic groups orient in the same direction and interdigitate with adjacent layers to generate hydrophobic regions. The hydrophilic faces of adjacent bilayers also face one another and can incorporate water molecules. The thickness of hydrophilic layers ranges from 3.2 to 3.4 Å, while the thickness of interdigitated layers increases with the size of the organic group.

**Stoichiometry 1:3 ( $\text{H}_3\text{TMA}$ :amine).** In principle, 1:3 stoichiometry offers the opportunity to generate honeycomb networks. As revealed by Figure 20a, motif A or B should be capable of propagating the trimesate anion into a honeycomb structure. Figure 20b reveals that the crystal structure of  $[\text{TMA}-[\text{dicyclohexylammonium}]_3$  exists as the anticipated honeycomb array.<sup>290</sup> The cyclohexyl moieties, which are omitted for the sake of clarity, effectively prevent interpenetration by capping the 13 Å cavities that are present within the honeycomb structure. If the



**Figure 20.** Modular honeycomb network sustained by BTC trianions and secondary alkylammonium cations: (a) schematic representation of the hydrogen-bonding pattern and (b) space-filling illustration of the crystal structure of  $[(\text{BTC}^{2-})(\text{NH}_3(\text{C}_6\text{H}_{12})^+)_2]$ .

solvent is changed, a honeycomb network based upon the other supramolecular synthon is generated,<sup>293</sup> and it has been reported that this form of the honeycomb network will self-assemble at the air-water interface. The modular nature of this structure permits replacement of the cyclohexyl moieties by other moieties. In this context, alkyl groups that are less sterically demanding (e.g., *n*-alkyl) have also been incorporated into the motif in Figure 20a. Interpenetration occurs in these structures.

**Guanidinium Sulfonates.** A series of related structures that are based upon two-dimensional layers resulting from hydrogen bonding of the trigonal guanidinium cation,  $\text{C}(\text{NH}_2)_3^+$ , and organic sulfonate ions  $\text{RSO}_3^-$  has been extensively studied by the Ward group<sup>176,238,240,295–302</sup> (Scheme 14).

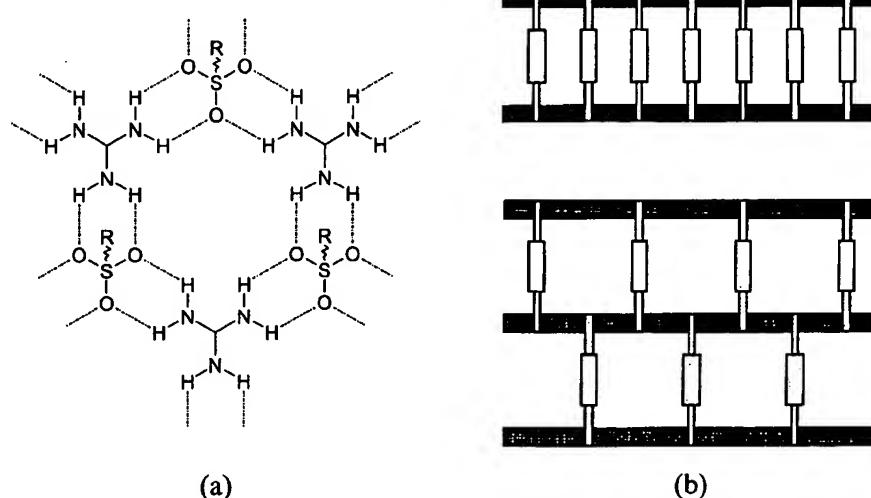
Interdigitation of the organic substituent of the sulfonate ions on adjacent layers and ionic hydrogen-bonding predictably leads to a broad series of laminar architectures. It should be noted that there are several key differences between guanidinium sulfonates and alkylammonium trimesates. (1) There exists only one ancillary organic functional group per sulfonate ion compared to up to two ancillary functional groups per ammonium cation. (2) The anion is functionalized rather than the cation. (3) In one sense, the alkylsulfonates are more versatile since they can exhibit architectural (i.e., supramolecular) isomerism so as to generate either bilayer or clay-like architectures. To generate a clay-like architecture, organic groups must orient above and below each layer as illustrated by Scheme 15. The steric demands of the organic group appear to determine whether they orient in the same direction (i.e., a bilayer structure) or alternate above and below the layer (i.e., a clay-like structure).

### C. 3D Networks

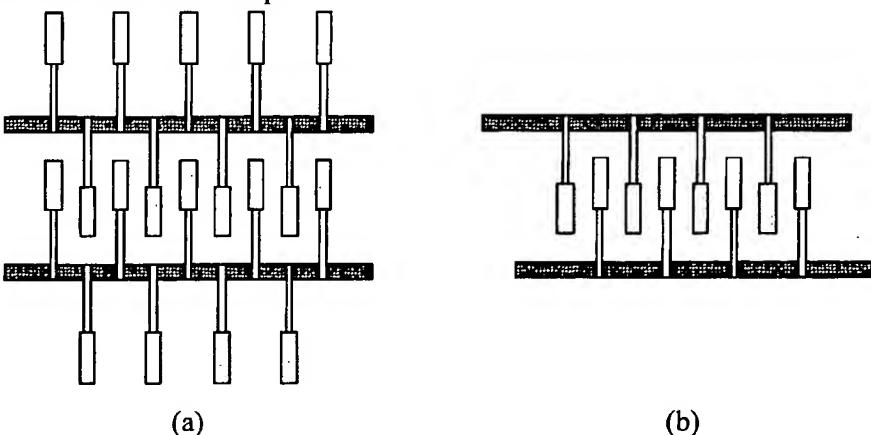
#### 1. Self-Assembled Hydrogen-Bonded Diamondoid Networks

A report by Ermer<sup>86</sup> on the structural characterization of adamantine-1,3,5,7-tetracarboxylic acid and its implications represented a watershed for crystal engineering. Ermer's study was followed by a flurry of activity into design from first principles of both organic diamondoid networks and metal-organic diamondoid coordination polymers. The carboxylic

**Scheme 14. Schematic Illustration of the Key Structural Features of Guanidinium Sulfonates: (a) Hexagonal Channels that Form 2D Honeycomb Networks and (b) Two Extended Structures (2D and 3D) that Can Result from the Self-assembly of Guanidinium Cations with Disulfonates Anions**



**Scheme 15. Schematic Illustrating Two Possible Modes of Interdigitation for Guanidinium Sulfonates: (a) Clay-like, Induced by Sterically Demanding Functional Groups and (b) Bilayer Architecture, Typically Observed for Smaller Functional Groups**



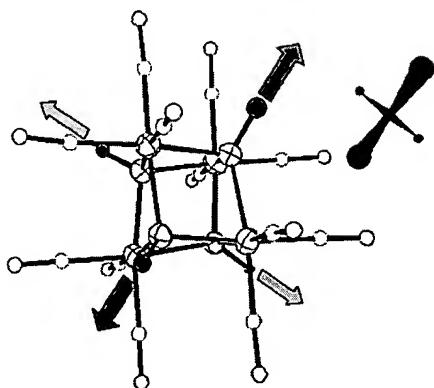
acid groups of adamantane-1,3,5,7-tetracarboxylic acid are tetrahedrally oriented. It is therefore unsurprising that they self-assemble via the hydrogen-bonded carboxylic dimer supramolecular synthon to afford an infinite diamondoid network. Each network possesses cavities that could accommodate a large roughly spherical guest, or guest aggregate, of roughly 12 Å in diameter. However, these cavities are filled by five independent networks that interpenetrate in such a way that the crystal structure is densely packed, and consequently, guest inclusion is precluded. As subsequent studies have revealed, interpenetration is a widespread phenomenon in diamondoid networks and occurs in many other organic and metal-organic structures that would otherwise have large cavities or channels. An interpenetrated diamondoid architecture is also exhibited by methanetetraacetic acid, for which the cavities generated are approximately 10 Å in diameter.<sup>87</sup> As would be expected, methanetetraacetic acid exhibits a lower degree of interpenetration: 3-fold. 2,6-dimethylidine-adamantane-1,3,5,7-tetracarboxylic acid also forms a hydrogen-bonded diamondoid structure, but it exhibits a much lower degree of interpenetration

than its unsubstituted precursor. The 2-fold "double diamondoid" architecture is not as densely packed, and it can therefore act as a host and enclathrate guest molecules.<sup>86</sup>

Wuest demonstrated that the pyridone moiety also generates a hydrogen-bonded supramolecular synthon that is suitable for building extended arrays.<sup>89,303,304</sup> Remarkably, methanetetra(6-phenylethynyl-2-pyridone) exhibits a diamondoid network, 7-fold interpenetration, and cavities large enough to enclathrate butyric or valeric acid.<sup>89</sup> Wuest introduced the concept of "tectons" to describe molecules that inherently possess the molecular structure and intermolecular recognition features to predictably self-assemble into crystalline networks. This study was followed by studies that demonstrated that there are several other examples of diamondoid networks that can be sustained by the pyridone moiety.<sup>305,306</sup>

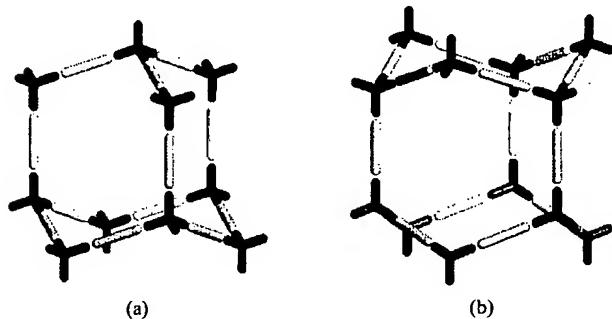
## 2. Modular Self-Assembly of Hydrogen-Bonded Diamondoid Networks

As discussed earlier, modular self-assembly relies upon two molecular components that are not individually capable of self-assembly and can be invoked



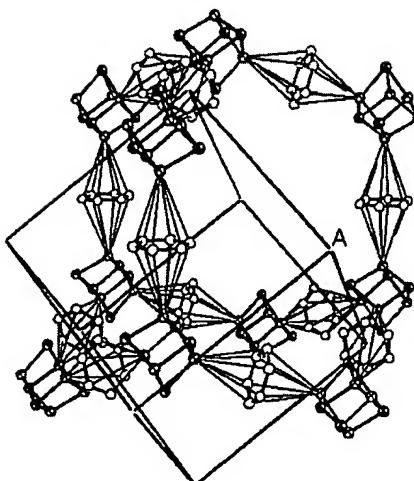
**Figure 21.**  $[\text{Mn}(\mu_3\text{-OH})(\text{CO})_3]_4$ : a cubane-like cluster possessing perfect  $T_d$  symmetry that represents a prototypical example of a tetrahedral hydrogen-bond donor.

**Scheme 16. Schematic Illustration of the Two Types of Diamondoid Architecture: (a) Cubic and (b) Hexagonal**



to understand coordination polymers or multiple-component hydrogen-bonded networks.<sup>90</sup> There are significant differences between the types of tetrahedral moiety that can sustain networks that have been self-assembled from a single component vs networks that have been self-assembled from multiple components. The most fundamental difference between the two types of structure is that the tetrahedral component that sustains single-component self-assembled architectures would not ordinarily be able to sustain modular architectures and vice versa. In the case of the former, the tetrahedral moieties must be self-complementary and there is only one component necessary for self-assembly to occur. This means, for example, that both hydrogen-bond donors and hydrogen-bond acceptors must be present in the same molecule. In the case of the latter, the tetrahedral node must be either an acceptor or a donor of hydrogen bonds and the linker or spacer must be complementary. Both components are necessary, and there must be a 1:2 ratio in order for the diamondoid architecture to self-assemble. Scheme 16 illustrates the difference between the two types of diamondoid networks.

An example of a node that is suitable for modular self-assembly is the cubane cluster  $[\text{Mn}(\mu_3\text{-OH})(\text{CO})_3]_4$ ,<sup>307</sup> which possesses perfect  $T_d$  symmetry and has four strong hydrogen-bond donors and no strong hydrogen-bond acceptors (Figure 21). This tetrahedral hydrogen-bond donor forms diamondoid cocrystals with a wide range of obvious and, in some cases, not so obvious spacer molecules. A “not so obvious”



**Figure 22.** Illustration of the crystal structure and diamondoid cavity generated in  $[\text{Mn}(\mu_3\text{-OH})(\text{CO})_3]_4 \cdot 2\text{benzene}$ .

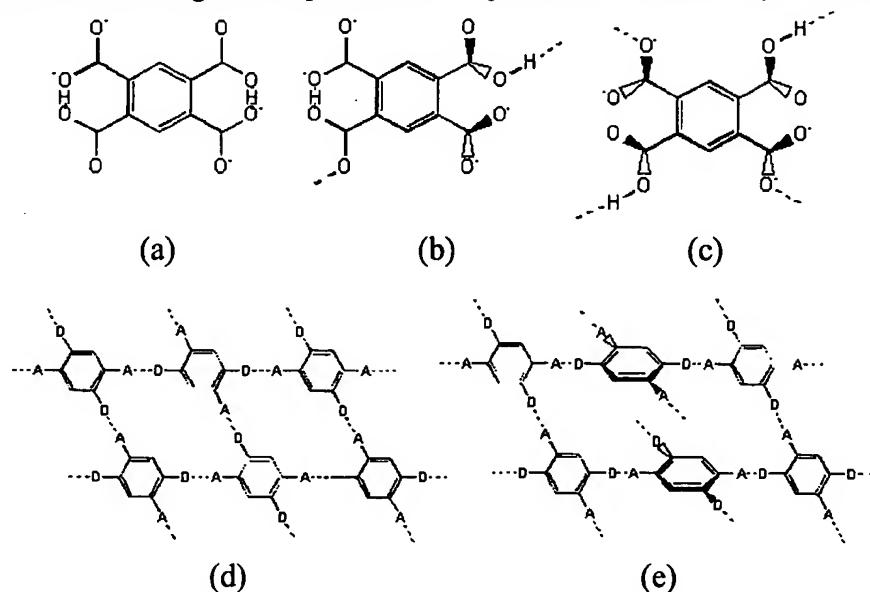
structure is that formed when  $[\text{Mn}(\mu_3\text{-OH})(\text{CO})_3]_4$  is cocrystallized with benzene.<sup>308</sup> A 2-fold diamondoid structure is sustained by  $\text{OH}\cdots\pi$  hydrogen bonds, and the tetrahedral symmetry of the node is observed in the crystallographic sense since  $[\text{Mn}(\mu_3\text{-OH})(\text{CO})_3]_4 \cdot 2\text{benzene}$  crystallizes in the cubic space group  $Pn-3m$  with  $z = 2$ . As revealed by Figure 22, which illustrates an adamantine portion of the structure, a large cavity is generated and this facilitates interpenetration of a second diamondoid network.

The use of transition metals or transition-metal clusters to act as nodes for the modular self-assembly of diamondoid networks that are sustained by coordinate covalent bonds is also well established. Such architectures are of more than aesthetic appeal, and they have resulted in a class of compounds with interesting bulk and functional properties. Metal-organic diamondoid structures in which the spacer moiety has no center of inversion are predisposed to generate polar networks since there would not be an inherent center of inversion. Pyridine-4-carboxylic acid, isonicotinic acid, is such a ligand, and bis(isonicotinato)zinc exists as a 3-fold diamondoid structure that is both thermally stable and inherently polar.<sup>228</sup> It exhibits SHG activity that is three times higher than the commercially relevant NLO material KDP.<sup>309,310</sup>

There are also supramolecular synthons that do not rely upon hydrogen bonds. In this context,  $\text{N}\cdots\text{Br}$  interactions were exploited to propagate a diamondoid network in the cocrystal formed by carbon tetrabromide and hexamethylenetetraamine. This structure also represents a different but equally effective form of the modular approach: two tetrahedral nodes with one possessing donor functionality and the other acceptor functionality only. The structure of the cocrystal formed by carbon tetrabromide and hexamethylenetetraamine exhibits 2-fold interpenetration and does not enclathrate solvent or guest.<sup>311</sup>

### 3. Other 3D Hydrogen-Bonded Networks

Although there are many examples of organic crystals that can be defined as 3D networks, few of

**Scheme 17. Schematic Illustrating Five Supramolecular Synths Possible for Pyromellitate Dianions**

them are predictable or even rational in the same sense as diamondoid networks. Trimesic acid, H<sub>3</sub>TMA, is an interesting exception and was discussed earlier in the context of 2D structures. H<sub>3</sub>TMA represents a prototypal molecule in the context of hydrogen bonding and generates extended structures when pure, partially deprotonated, in coordination polymers or in cocrystals. Anionic derivatives of H<sub>3</sub>TMA self-assemble into honeycomb grids via O—H···O<sup>-</sup> hydrogen bonds.<sup>280–282,312,313</sup> Pyromellitic acid, 1,2,4,5-benzenetetracarboxylic acid, H<sub>4</sub>PMA, has been less widely explored than H<sub>3</sub>TMA. It has been utilized as a ligand in coordination polymer networks,<sup>294</sup> and very few organic structures containing H<sub>4</sub>PMA or its derivatives are known. We anticipated that doubly deprotonated H<sub>4</sub>PMA would self-assemble via dicarboxylate hydrogen bonds to form 0D (two intramolecular hydrogen bonds), 1D (one intramolecular and one intermolecular hydrogen bond), or 2D/3D (two intermolecular hydrogen bonds) networks (Scheme 17). H<sub>2</sub>PMA<sup>2-</sup> anions exhibit all four of these supramolecular isomers depending upon the polymorph or the counterion.<sup>314</sup> The 3D structure occurs because H<sub>2</sub>PMA<sup>2-</sup> moieties orient in such a manner that they form hydrogen bonds to the next layer. The network can be described as a framework built from square building blocks that alternate parallel and perpendicular with respect to one another. This network can therefore be regarded as an organic analogue of NbO.<sup>66</sup>

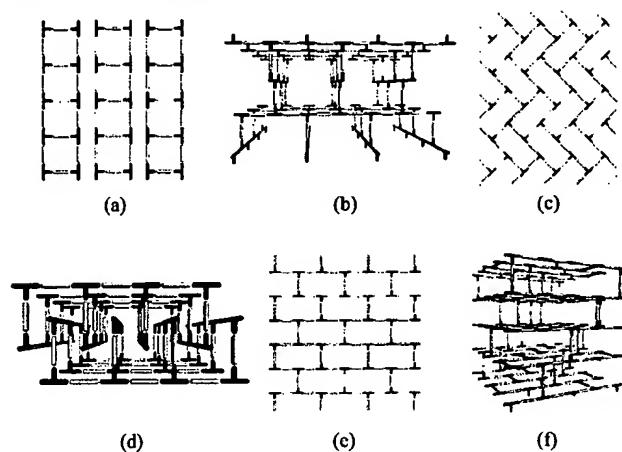
It should be obvious that all 2D networks must, in the absence of solvent or intercalated guest, engage in noncovalent interactions with the layers above and below. The possibility of exploiting a combination of molecular recognition modes represents a particularly attractive approach to control crystal packing since it places no restrictions in terms of the type of chemical components that can be rationally incorporated into crystalline phases. In this context, Fowler and Lauher<sup>19,315–320</sup> illustrated how it is possible to use hydrogen bonding to control interactions between 1D networks, or  $\alpha$ -networks, and to thereby yield

predictable 2D networks or  $\alpha$ -networks. If the sheets are designed to be self-complementary in the third dimension, then a predictable 3D network or  $\gamma$ -network can result. Fowler and Lauher demonstrated not only that such a strategy is viable, but that it can offer a degree of control over stacking of layers such that the interlayer components are positioned within the limits of the topochemical principle. They were thereby able to effect solid-state reactions upon appropriate perturbation. When coupled with other advances in this context, including recent reports<sup>17,19</sup> that demonstrate how discrete aggregates may also afford components that are positioned within the topochemical boundaries, it should be clear that crystal engineering involving multiple types of molecular recognition offers significant implications for solid-state synthesis and solvent-free, green chemistry.

#### **IV. Supramolecular Isomerism and Polymorphism**

The existence of supramolecular isomerism might be seen as a problem from a design perspective since it necessarily implies that there will be superstructural diversity for a given molecular building block. However, there is another way to look at this matter. It is also possible to view supramolecular isomerism as an opportunity to gain a better fundamental understanding of the factors that influence crystal nucleation and growth. Such a linkage can be justified as follows. (1) If one invokes the concept of supramolecular isomerism, then it should become apparent that it represents a significant limitation on the number of possible superstructures (i.e., discrete structures or 1D, 2D, or 3D networks) that can occur for a given molecular building block. Therefore, one can invoke a study on supramolecular isomerism or polymorphism with the assumption that self-assembly means that there will only be a finite number of architectures that are feasible for a given molecular species. This assumption will be based upon crystals being the result of directional

**Scheme 18. Schematic Illustration of the Six Supramolecular Isomers Reported for T-Shaped Nodes Linked by Linear Bifunctional Exodentate Ligands: (a) 1D Ladder, (b) 3D Lincoln Logs, (c) 2D Herringbone, (d) 2D Bilayer, (e) 2D Brick Wall, and (f) 3D Frame**



supramolecular synthons, the fundamental precept of crystal engineering. (2) The ability of the crystal engineer to design a molecular building block that is predisposed toward the formation of supramolecular isomers provides an ideal opportunity for design of supramolecular isomers and, perhaps more importantly, for learning how to control supramolecular isomers. At the very least, it will be possible to develop "recipes" that invoke crystallization conditions, templates, and/or solvents to favor or disfavor a particular supramolecular isomer.<sup>321,322</sup> (3) The concepts of self-assembly, crystal engineering, and networking provide clear implications for gaining a better fundamental understanding of polymorphism since polymorphism can be regarded as a subset of supramolecular isomerism. (4) It should be clear that to gain a better understanding of supramolecular isomerism and polymorphism, it is a requirement that full structural characterization of compounds be conducted. This means an in-depth analysis of crystal packing and intermolecular contacts as well as measurement of physical properties.

To illustrate the linkage between crystal engineering, supramolecular isomerism, and polymorphism, we shall consider three types of supramolecular isomerism and demonstrate how analogies can be readily drawn between coordination polymers and organic networks.

### A. Structural Supramolecular Isomerism

That structural supramolecular isomerism can have profound implications for structure and properties is exemplified by the range of structures that has thus far been observed in coordination polymers that are generated by one of the simplest building blocks and stoichiometries: 1:1.5 stoichiometry, mer-metal, and linear spacer ligand. These building blocks can be regarded as being based upon self-assembly of T-shaped nodes. There already exists a surprisingly diverse range of structures that have been observed in this context. Scheme 18 illustrates the supramo-

lecular isomers that have thus far been observed: ladder<sup>91,178</sup> (A), brick wall<sup>204</sup> (B), 3D frame or "Lincoln Logs"<sup>236,237</sup> (C), bilayer<sup>213</sup> (D), herringbone<sup>210</sup> (E),<sup>78,211,212</sup> and another version of a 3D frame<sup>177</sup> (F). Three of the isomers A,<sup>178</sup> D,<sup>213</sup> and F<sup>177</sup> have been observed for the same asymmetric unit for metal = Co(NO<sub>3</sub>)<sub>2</sub> and ligand = bipy, and the other three have been seen in similar compounds which use bipy or extended analogues as "spacer ligands".

The following points should be noted about such structures. (1) These compounds are not true polymorphs since guest or solvent molecules are present in the lattice. However, neither are they solvates in the conventional sense. (2) The diversity of network structures and hence bulk properties is remarkable. (3) None of these architectures occurs naturally in minerals. (4) The network structures themselves are entirely predictable based upon simple structural considerations. (5) Some of these structures can occur from the same building blocks under almost identical crystallization conditions.

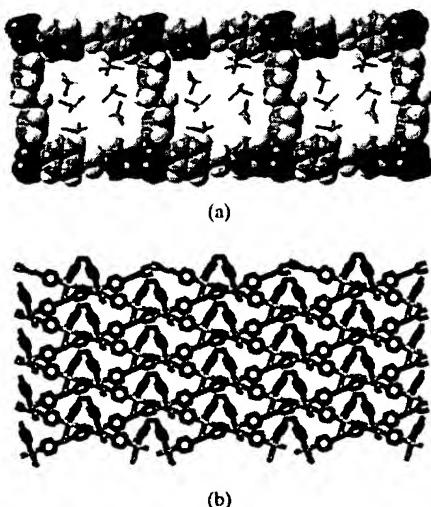
It is possible to draw direct analogies with polymorphism in organic crystals. For example, a similar approach based upon networks can be used to analyze the packing in organic compounds. A recent paper highlighted this situation in the context of 2-amino-5-nitropyrimidine, a compound that exhibits three readily available polymorphs, all of which have distinct hydrogen-bonded networks.<sup>323</sup> Etter's study concerning carboxylic acids<sup>88</sup> and how they can self-assemble to form either head-to-tail chains or centrosymmetric dimers also illustrates how one can rationalize polymorphism based upon supramolecular isomers and networks.

In summary, it seems likely that use of appropriate templates or guest molecules facilitates recipes that can be used to reliably generate all supramolecular isomers that are possible for a given node. Therefore, one might assert that there are a finite number of superstructures possible for a given molecular moiety and that it will eventually be possible to determine the crystallization conditions under which each one will occur.

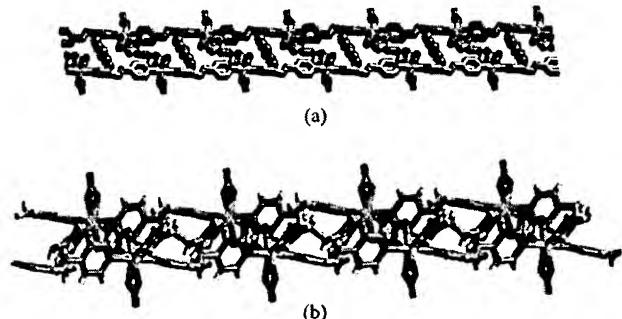
### B. Conformational Supramolecular Isomerism

Flexibility in ligands can lead to subtle or dramatic changes in architecture. For example, 1,2-bis(pyridyl)ethane, bipy-eta, can readily adapt *gauche*- or *anti*-conformations. In the case of [Co(bipy-eta)<sub>1.5</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub>, which contains a T-shaped node, infinite molecular ladders which contain six molecules of chloroform per cavity exist as the most commonly encountered architecture (Figure 23a).<sup>186</sup> In such a situation, all "spacer ligands" are necessarily *anti*. However, under certain crystallization conditions (e.g., solvent MeCN or dioxane), a bilayer architecture is obtained with two *anti*- and one *gauche*-spacer ligand per metal atom (Figure 23b).

The bilayer architecture can contain solvent molecules such as MeCN or can collapse on itself in the absence of solvent.<sup>44</sup> This more subtle form of supramolecular isomerism occurs if [Co(bipy-eta)<sub>1.5</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> is crystallized in the absence of a suitable guest or solvent.<sup>217</sup> Figure 24 reveals how [Co(bipy-



**Figure 23.** Illustrations of two structures observed for  $[Co(bipy-\eta)_{1.5}(NO_3)_2]$ : (a) ladder in which all bipy- $\eta$  ligands adapt an *anti*-orientation and (b) bilayer in which bipy- $\eta$  ligands adapt *anti*- and *gauche*-orientations in a 2:1 ratio.



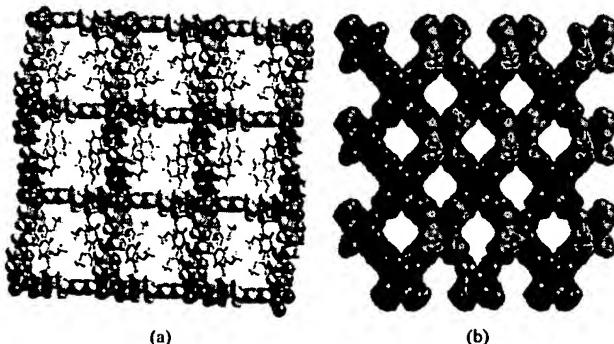
**Figure 24.** Illustrations of crystal structures of  $[Co(bipy-\eta)_{1.5}(NO_3)_2]$  cocrystallized with (a) MeCN and (b) no solvent of crystallization. Note how the cavities collapse in the absence of the adsorbed solvent.

$\text{eta}_{1.5}(NO_3)_2$ , collapses to close the cavity that exists when crystallized from MeCN.<sup>44</sup> Note the difference in torsion angles between the two compounds. A similar situation occurs in compounds based upon a longer bis-pyridyl ligand, 1,4-bis(4-pyridyl)methyl)-2,3,5,6-tetrafluorophenylene, 2. When 2 is complexed to Cd to form compounds of formula  $[\text{Cd}(2)_2(NO_3)_2]$ , three very different supramolecular isomers have been observed depending upon the nature of guests or templates: 1D chains, 2D sheets, and 3D diamondoid networks.<sup>324</sup>

A dramatic illustration of how conformational variability can influence crystal packing in organic compounds is illustrated by the compound 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophencarbonitrile. This compound exists in at least six polymorphic phases. The primary difference between the six phases lies with the torsion angle between the thiophene moiety and the *o*-nitroaniline fragment, which varies from  $21.7^\circ$  to  $104.7^\circ$ .<sup>55</sup>

### C. Catenane Supramolecular Isomerism

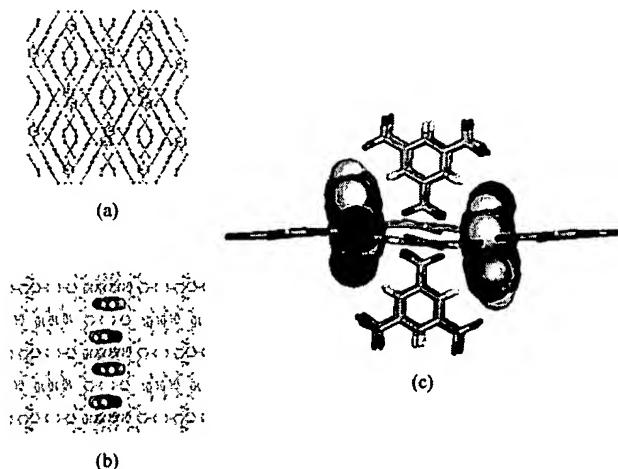
The existence of independent interpenetrating networks is surprisingly common if relatively large



**Figure 25.** Illustrations of two crystal structures of the square grid coordination polymer  $[\text{Ni}(bipy-\eta)_2(NO_3)_2]$ : (a) with included guest molecules and (b) interpenetrated networks.

cavities are generated within a network. A thorough review of this subject in the context of coordination polymers was recently published by Batten and Robson.<sup>58</sup> The existence of interpenetration has been regarded as a factor that mitigates strongly against the generation of stable open framework structures. However, it is becoming clear that appropriate use of templates can afford either open framework or interpenetrated structures for the same network. This is exemplified by the prototypal diamondoid and square grid networks  $\text{Cd}(\text{CN})_2$  and  $M(\text{bipy})_2\text{X}_2$ . Both of these compounds have been prepared as interpenetrated and noninterpenetrated forms. Furthermore, some interpenetrated structures can also be regarded as open framework since if interpenetration will not necessarily afford close-packing. Interpenetrated structures can still contain channels large enough to hold, for example, aromatic guests. Such is the case for square grid networks based upon ligands such as bipy- $\eta$ . Figure 25 reveals how either open framework square grid or interpenetrated square grid structures can be readily generated for the same square grid network.<sup>200</sup> Both compounds contain square grids of formula  $[\text{Ni}(bipy-\eta)_2(NO_3)]_n$ . As would be expected, the compound illustrated in Figure 25a,  $[\text{Ni}(bipy-\eta)_2(NO_3)]_n$ , exhibits clay-like properties and can desorb and adsorb guests. Crystallinity is lost, but the square grid architecture retains its integrity below  $220^\circ\text{C}$ . The interpenetrated analogue is illustrated in Figure 25b and is effectively a 3D architecture that is built by interpenetration of square grids. This compound has a more rigid structure than its noninterpenetrated form and behaves like a zeolitic solid rather than a clay-like solid. Both compounds are stable to loss of guest, but the former loses crystallinity upon loss of guest.

Organic networks are also capable of exhibiting interpenetration, and in this context  $\text{H}_3\text{TMA}$  represents a prototypal example. As discussed earlier,  $\text{H}_3\text{TMA}$  is predisposed to generate honeycomb sheets with large cavities. Three phases of  $\text{H}_3\text{TMA}$  have thus far been characterized. In two of these phases, one of which is pure  $\text{H}_3\text{TMA}$ , 3-fold interpenetration of the individual hexagonal cavities occurs.<sup>282</sup> In pure  $\text{H}_3\text{TMA}$ , the honeycomb networks are puckered in such a manner that small cavities are generated.<sup>280</sup> These cavities can hold small molecules, including



**Figure 26.** Illustration of the  $\alpha$ -polymorph of BTC that illustrates how BTC can sustain the enclathration of *p*-nitroaniline: (a) view of the 10-fold interpenetrated puckered honeycomb networks, (b) view of a single BTC network with 3-fold interpenetration per cavity and incorporation of *p*-nitroaniline in "pockets", and (c) perspective view of two *p*-nitroanilines situated in a single cavity, surrounded by the three interpenetrating networks.

halogens<sup>312</sup> and *p*-nitroaniline.<sup>325</sup> The structure of the inclusion compound formed between H<sub>3</sub>TMA and *p*-nitroaniline is illustrated in Figure 26. The other interpenetrated phase of H<sub>3</sub>TMA contains flat sheets, and it therefore contains infinite 1D channels.<sup>281</sup> The noninterpenetrated phase of H<sub>3</sub>TMA, illustrated in Figure 14, is formed when long-chain alkanes are used during the crystallization process.

A honeycomb network is also generated when H<sub>3</sub>TMA is cocrystallized with bipy. This structure exhibits interpenetration in 2D to form a novel carpet-like architecture.<sup>283</sup> However, the noninterpenetrated form remains to be isolated.

The results described above all suggest that interpenetration can be avoided if appropriate templates are used during the crystallization. It is therefore reasonable to see interpenetration as another example of supramolecular isomerism, one that can be controlled by use of guest or template molecules during crystallization.

## V. Potential Applications

A considerable amount of research into understanding the nature and predictability of supramolecular synthons remains to be conducted. An enhanced database concerning supramolecular synthons in the broad context would also assist our fundamental understanding of solution chemistry and biochemistry. Nevertheless, it is clear that there are a number of applications of crystal engineering that could be realized in the short term. Several of these are summarized below. (1) From a supramolecular perspective, binary compounds represent an illustration of how one might exploit the modular approach to design new supermolecules, especially in the solid state. It is reasonable to assert that supramolecular synthesis of new classes of cocrystal and modular solid offers potential to increase the known range of crystalline materials by two or three orders of

magnitude and to facilitate combinatorial approaches to materials science. For example, if one were to only consider cocrystals that are sustained by hydrogen bonding, a wide range of compositions exists that remain to be explored. It is perhaps sobering to realize that, at least in principle, molecules that are deficient in hydrogen-bond acceptors are inherently prone to form supermolecules with molecules that contain excess hydrogen-bond acceptors. Even if one considered only simple examples such as pyridines, there are many permutations for formation of binary compounds. If one were to study, for example, 20 pyridines and 20 carboxylic acids, then one would expect 400 new binary compounds with predictable composition and structure. Such a strategy could be important in the context of supramolecular derivatives of drugs and functional materials (i.e., modification of bulk properties without changing the molecular structure of the active species) or they could serve as precursors to covalent products, including polymers. Such an approach has already been effective in formulation of polaroid film.<sup>326</sup> There also exists the possibility of rationalizing certain types of host–guest structures as being based upon topologically complementary networks.<sup>241,243</sup> Such compounds are also based upon self-assembly and might be prototypal for large numbers of related structures. (2) It is already established that solvent-free synthesis, green chemistry, offers many potential advantages, including cost and environmental benefits.<sup>13,14</sup> Cocrystallization of substrates and subsequently conducting reactions in the solid state offers the opportunity for very careful control over regio- and stereochemistry. It is also possible that supramolecular arrays could act as precursors to new classes of 2D and 3D covalent polymers.<sup>327</sup> (3) New classes of adsorbent, "organic and metal–organic clays and zeolites" represent an area in which considerable progress has already been made. Such compounds offer clear potential for the following: efficient, cost-effective alternatives to current methods of enantiomeric separations, new materials for separation of gases, liquids, and solutes, new industrial heterogeneous catalysts, new drug delivery matrixes (e.g., matrix for oral delivery of otherwise unstable drugs), a new generation of chemical sensors, and new storage matrixes for gases such as methane. Recent results indicate that synthetic metal–organic polymers can offer high levels of thermal stability and can supersede zeolites in terms of surface area and capacity for small guest molecules.<sup>76,81</sup> (4) The rational design of polar materials for use in materials science also represents an aspect of crystal engineering that has already provided promising developments. Unfortunately, in most organic crystals, antiparallel architectures predominate, thereby canceling dipoles of highly polarizable molecules and mitigating against optimization of bulk polarity. Fortunately, there now exists an extended range of modular, open framework organic and metal–organic solids. Many of these compounds contain architectures (e.g., square grid, honeycomb, octahedral) that favor incorporation of polar strands into channels, thereby reducing the driving force for

antiparallel alignment. Results obtained by the groups of Hollingsworth<sup>328–332</sup> and Hulliger et al.<sup>333–340</sup> suggest that such compounds, in particular channel-type inclusion compounds, hold considerable promise in the context of the design of solids that possess fine-tunable bulk polarity. Diamondoid networks also offer considerable potential in this context since tetrahedral nodes do not contain a center of inversion.<sup>90</sup> The recent results of Lin's group indicate that diamondoid networks can couple high thermal stability with high SHG activity.<sup>228,229</sup> (5) Metal–organic polymers offer considerable potential in the context of molecular magnetism, semiconductors, and conductors.<sup>341–347</sup> Once again, the possibility of design and fine-tuning becomes apparent when one develops structures with predictable architectures that are based upon paramagnetic metal ions. The presence of guest molecules can be a desirable feature as it would be expected to offer a degree of fine-tuning that is not inherently present in single-component compounds.

## VI. Conclusions and Future Directions

*"The peasant who wants to harvest in his lifetime cannot wait for the ab initio theory of weather", H. G. von Schnering (1981).*

The fundamental precept of crystal engineering is that all information necessary for design of extended 1D, 2D, and 3D structures is already present at the molecular level in existing chemical species. Recent advances in our understanding of supramolecular chemistry and supramolecular synthons have been aided by the advent of CCD diffractometers coupled with ever more powerful visualization and analysis tools. It should therefore be unsurprising that control over supramolecular architectures, also known as molecular tectonics,<sup>348</sup> has advanced rapidly in recent years. That these tools are now routinely available means that an even more concerted and systematic approach to gaining an understanding of the subtle factors that control architectures in the solid state is feasible. The rational design of supramolecular structure necessarily relies upon invoking the concepts of self-assembly, in effect supramolecular synthesis, and exploits noncovalent forces as varied as the following: (1) hydrogen bonding, including both strong hydrogen bonding (e.g., O–H–O) and weak hydrogen bonding (e.g., C–H–O and even C–H–π), (2) coordinate covalent bonds (e.g., metal–organic polymers), (3) electrostatic and charge-transfer attractions, and (4) aromatic π-stacking interactions.

These principles of crystal engineering and supramolecular synthesis have thus far been used to design, isolate, and characterize a number of novel network structures that are prototypal because they are based upon modular components. However, these networks are typically based upon relatively small molecular components and the number and chemical type of components is typically restricted. It is in these two areas that there appears to be almost unlimited potential for supramolecular synthesis. In the context of coordination polymer networks, a recent review indicates how wide the range of chemi-

cal components and accessible network motifs has become.<sup>215</sup> However, the scale of these structures is such that cavities and channels are on the order of 10 Å and, to date, each cavity is identical. Careful selection of appropriate substrates or components and ever more control over crystal packing will offer the potential for rational design of an even more extensive array of modular (i.e., binary, ternary, or even higher order) structures than those that are currently available. In particular, judicious choice of secondary building units,<sup>84</sup> supermolecules, or biomolecules as templates and nodes should afford composite materials with nanoscale dimensions and cavities. The same is likely to be true concerning the rational development of structures that are based upon components that are at first glance incompatible. A number of examples of pure crystalline compounds that are based upon metal–organic polymers and metal oxide clusters have been reported in recent years.<sup>197,289,349,350</sup> Such composite materials would represent "uncharted territory", but they are a natural outgrowth of modular approaches to chemistry and now appear to be at hand. In essence, suprasupermolecular<sup>351</sup> synthesis in the solid state is likely to develop considerably further and, whereas prediction of crystal structures remains an elusive goal that will continue to be addressed, it does not preclude short-term applications of crystal engineering in a number of important areas. H. G. von Schnering's comments therefore seem particularly appropriate to summarize the current opportunities for crystal engineering and design.<sup>352</sup>

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## Nanoballs: nanoscale faceted polyhedra with large windows and cavities

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**Self-assembly of molecular polygons by linking their vertices provides nanosized faceted polyhedra that are porous, contain chemically accessible sites on their facets, are chemically robust, neutral and soluble in common laboratory solvents.**

In recent years chemists have developed synthetic design strategies that are based upon the concepts of self-assembly. This supramolecular approach to synthesis, a 'bottom-up'<sup>1</sup> approach to nanoscience, has afforded a new generation of discrete, high molecular weight compounds. These compounds are exemplified by nanoscale spheroid architectures that are based upon Platonic (regular) and Archimedean (semi-regular) solids.<sup>2-9</sup>

Nanoscale versions of Platonic and Archimedean solids have been prepared by one of two approaches: edge-sharing of molecular polygons,<sup>7</sup> or connection of appropriately designed molecular vertices by linear bifunctional rod-like ligands.<sup>10</sup> Edge-sharing of molecular polygons affords closed convex polyhedra whereas connection of vertices generates open structures that are the edge-skeletons of polyhedra. However, there exist other examples of uniform polyhedra<sup>11,12</sup> that to our knowledge remain unexplored in the context of synthetic chemistry. Uniform polyhedra include prisms and antiprisms, polyhedra having star faces and vertices, and polyhedra with both concave and convex faces.<sup>13</sup> In particular, there are nine uniform polyhedra that are closely related to Platonic and Archimedean solids but differ in that their convex faces can be constructed by linking the vertices of regular polygons. Such structures are termed faceted polyhedra<sup>14</sup> since they must contain both open (concave) and closed (convex) faces (*i.e.* faceting).

As revealed by Fig. 1 there are three faceted uniform polyhedra that can be generated by linking the vertices of squares and which one occurs will be strongly influenced by the angle subtended by the 'spacer' moiety that links the vertices: *cubohemioctahedron* (90°) < *small rhombihexahedron* (120°) < *small rhombidodecahedron* (144°). Therefore, judicious control of the angle subtended by the vertices of the squares should afford control over which polyhedron will result. The molecular squares that we have targeted for study are the previously reported metal-organic secondary building units<sup>15</sup> (SBUs)  $M_2(RCO_2)_4 A$ . A is illustrated in Fig. 2 and represents a ubiquitous SBU that is present in nearly 900 crystal structures in the Cambridge Structural Database (CSD).<sup>16</sup> It should be

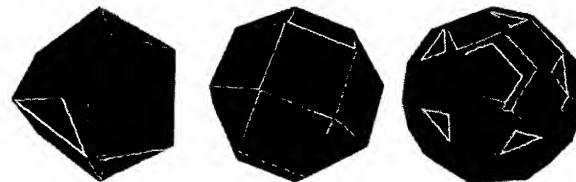


Fig. 1 The three types of faceted uniform polyhedra that can be generated by linking the vertices of squares only: *cubohemioctahedron*, *small rhombihexahedron* and *small rhombidodecahedron*.

noted that it has already been demonstrated that use of polycarboxylate ligands in  $M_2(RCO_2)_4$  (*e.g.* benzene-1,4-dicarboxylate<sup>17</sup> or benzene-1,3,5-tricarboxylate<sup>18</sup>) affords self-assembled infinite structures with predictable topology and relatively high thermal stability. It occurred to us that the angular bifunctional ligand benzene-1,3-dicarboxylate, bdc, which subtends an angle of 120°, offers the possibility of generating discrete nanoscale *small rhombihexahedra* or supramolecular isomers<sup>19</sup> in the form of novel infinite coordination polymers.

Nanoscale *small rhombihexahedra* 1, are formed by layering methanolic  $Cu(NO_3)_2$  and  $H_2bdc$  onto a solution of pyridine that contains templates such as nitrobenzene or 1,2-dichlorobenzene. Single crystals of  $[(L)(S)Cu_2(bdc)_2]_{12}$ , L = pyridine, S = methanol, 1a, form within hours. Alternatively, micro-crystals of 1a can be obtained quantitatively by direct mixing of the above reagents. The crystal structure of 1a† is illustrated in Fig. 3 and reveals that it can be described as being composed of vertex linked molecular squares (green) that self-assemble into *small rhombihexahedra*. 1a contains pyridine ligands that are axially bonded to the metal ions that lie at the exterior surface and MeOH ligands at the interior surface metal binding sites. The internal cavity has a volume of *ca.* 1 nm<sup>3</sup> that is easily large enough to encapsulate C<sub>60</sub>. To our knowledge, 1a represents the largest spheroid structure that has yet been crystallographically characterized. It has a molecular volume of > 10 nm<sup>3</sup> and a molecular weight of 6.80 kDa. 1 can also be formed for L = S = methanol, 1b. Thus far we have isolated two crystalline phases that contain 1b, a monoclinic and a cubic phase.†

An isomer of the *small rhombihexahedron*  $[(MeOH)_2Cu_2(bdc)_2]_{12}$  2 crystallizes under similar conditions with 2,6-dimethylpyridine, a non-coordinating base, present instead of pyridine. 2 is illustrated in Fig. 4 and the connectivity of the SBUs is different. 2 has a molecular weight of 6.23 kDa, a molecular volume of *ca.* 10 nm<sup>3</sup> and exhibits textbook hexagonal close packing. Molecular modelling indicates insignificant difference in terms of torsional strain between 1 and 2 (calculated using MSI Cerius<sup>2</sup> Minimizer module).

1 and 2 are distinguished by the following features: they are neutral and soluble in organic solvents; they are chemically robust because of the stability of the square SBU (confirmed by high resolution mass spectrometry); they are likely to be chemically diverse because A exists for so many metals,

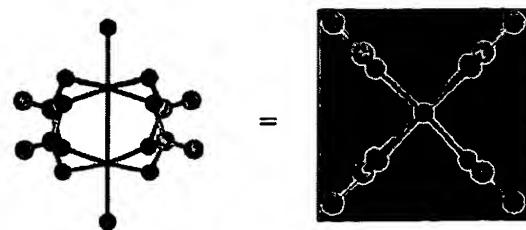
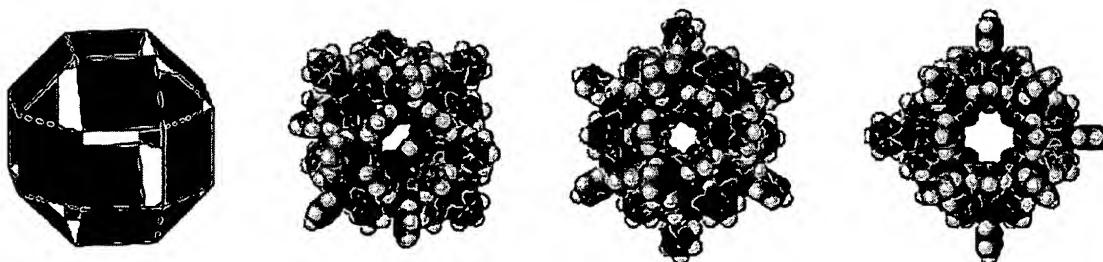
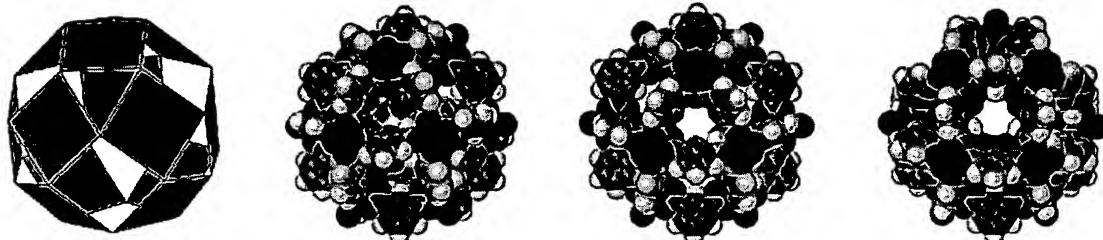


Fig. 2 The square SBU,  $M_2(RCO_2)_4 A$ , employed in this study. In the compounds described herein, A is schematically represented as a square (green).



**Fig. 3** Crystal structure of  $[(L)(S)Cu_2(bdc)_2]_{12}$ , L = pyridine, S = methanol, **1**. The schematic illustrates how linking of molecular squares generates the edge-skeleton of **1**. Note how the large bowl-shaped square and triangular windows provide access to the interior of **1**. Disordered solvent is found in these windows and in the  $1\text{ nm}^3$  internal cavity. There is high thermal motion and/or disorder in the ligands and the guest molecules but the structure of the core is well determined and unambiguous.



**Fig. 4** Crystal structure of  $[(S)_2Cu_2(bdc)_2]_{12}$ , S = methanol, **2**. The schematic illustrates the subtle differences between the connectivity in **1** and **2**.

including magnetically active and catalytically active metals; they have both internal and external sites that are suitable for further chemical modification. Indeed, it is possible to envisage **1** and **2** as the building blocks for much larger structures by acting as the node of infinite networks<sup>20</sup> or as the core of mesoscale dendritic structures; their interior cavities can be accessed via triangular or square windows, which are bowl shaped and contain organic guests. Loss of coordinated molecules occurs at higher temperatures. Furthermore, judicious selection of angular spacers in the presence of molecular polygons should ultimately generate all nine faceted polyhedra and their structural isomers.

## Notes and references

† *Crystallographic data:* intensity data for **1** and **2** were collected at 173 K on a Bruker SMART-APEX diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.7107\text{ \AA}$ ). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. Structures were solved using direct methods and refined by full-matrix least squares on  $|F|^2$ .<sup>11</sup> All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms.

*Crystal data:* for **1a**: triclinic,  $P\bar{1}$ ,  $a = 26.202(9)$ ,  $b = 27.756(10)$ ,  $c = 28.408(10)$   $\text{\AA}$ ,  $\alpha = 92.583(5)$ ,  $\beta = 96.393(5)$ ,  $\gamma = 92.643(5)$ ,  $V = 20483(12)$   $\text{\AA}^3$ ,  $Z = 2$ ,  $D_c = 1.279\text{ g cm}^{-3}$ ,  $\mu = 1.29\text{ mm}^{-1}$ ,  $F(000) = 7752$ ,  $2\theta_{\max} = 37.88^\circ$  ( $-23 \leq h \leq 23$ ,  $-25 \leq k \leq 25$ ,  $-25 \leq l \leq 20$ ). Final residuals (for 2529 parameters) were  $R1 = 0.1386$  for 10314 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.2849$ ,  $wR2 = 0.4220$ , GOF = 1.082 for all 31316 data. Residual electron density: 0.93 and  $-0.51\text{ e \AA}^{-3}$ .

For **1b** (monoclinic phase): monoclinic,  $C2/c$ ,  $a = 33.933(7)$ ,  $b = 36.925(7)$ ,  $c = 29.577(6)$   $\text{\AA}$ ,  $\beta = 93.4595(28)^\circ$ ,  $V = 36991.0\text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.353\text{ g cm}^{-3}$ ,  $\mu = 0.76\text{ mm}^{-1}$ ,  $F(000) = 15582$ ,  $2\theta_{\max} = 34.61^\circ$  ( $-28 \leq h \leq 28$ ,  $-30 \leq k \leq 30$ ,  $-24 \leq l \leq 13$ ). Final residuals (for 823 parameters) were  $R1 = 0.1353$  for 3512 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.3056$ ,  $wR2 = 0.4226$ , GOF = 1.031 for all 11089 data. Residual electron density: 0.66 and  $-0.44\text{ e \AA}^{-3}$ .

For **1b** (cubic phase): cubic,  $I\bar{m}\bar{3}\bar{m}$ ,  $a = 27.6895(17)$   $\text{\AA}$ ,  $V = 21229.8\text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.016\text{ g cm}^{-3}$ ,  $\mu = 1.24\text{ mm}^{-1}$ ,  $F(000) = 6454$ ,  $2\theta_{\max} = 46.50^\circ$  ( $-30 \leq h \leq 27$ ,  $-26 \leq k \leq 30$ ,  $-29 \leq l \leq 30$ ). Final residuals (for 100 parameters) were  $R1 = 0.0784$  for 996 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.1069$ ,  $wR2 = 0.2953$ , GOF = 1.138 for all 1501 data. Residual electron density: 0.83 and  $-0.44\text{ e \AA}^{-3}$ .

For **2**: hexagonal,  $P6_3/m$ ,  $a = b = 28.6458(19)$ ,  $c = 28.1649(26)$ ,  $V = 20015.2\text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.222\text{ g cm}^{-3}$ ,  $\mu = 1.32\text{ mm}^{-1}$ ,  $F(000) = 7326$ ,  $2\theta_{\max} = 45.11^\circ$  ( $-21 \leq h \leq 30$ ,  $-27 \leq k \leq 27$ ,  $-22 \leq l \leq 30$ ). Final residuals (for 728 parameters) were  $R1 = 0.1116$  for 4003 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.1837$ ,  $wR2 = 0.3416$ , GOF = 1.317 for all 8931 data. Residual electron density: 1.16 and  $-1.53\text{ e \AA}^{-3}$ .

CCDC 161338–161341. See <http://www.rsc.org/suppdata/cc/b1/b102714j> for crystallographic data in .cif or other electronic format.

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[14] This consideration in turn suggests that apparently stronger electronic interactions in the normal *meso*-*meso*-linked diporphyrins result from the rotational flexibility around the *meso*-*meso* single bond.  
[15] Selected  $^1\text{H}$  NMR signals of the pyridyl groups of (Z2) $_4$  in [D $_8$ ]THF: δ = 2.62, 3.11, 6.59, and 6.86 ppm.  
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## Crystal Engineering of a Nanoscale Kagomé Lattice\*\*

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What would the properties of materials be if we could really arrange the atoms the way we want them? Although this question is scientifically and technologically topical, it is a

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well-known excerpt from the Richard P. Feynman lecture "There's Plenty of Room at the Bottom".<sup>[1]</sup> Recent advances in our understanding of supramolecular chemistry offer promise that Feynman's dream will be realized since they have afforded design principles that have provided access to an array of new solid phases with specific and, in many cases, previously unknown molecular topologies. Indeed, as molecular scientists become ever more proficient at the supramolecular synthesis<sup>[2]</sup> of new compositions and structures, the question that might now be posed is: "in what manner do we want to arrange the atoms?" In the context of magnetic materials, theorists have provided chemists with an array of target lattices,<sup>[3]</sup> and synthetic chemists have developed new strategies for the generation of novel networks that contain magnetic components.<sup>[4-7]</sup> Spin-frustrated lattices represent attractive targets that are exemplified by the antiferromagnetic Kagomé lattice.<sup>[8]</sup> Herein we present the synthesis, crystal structure, and magnetic properties of, what is to our knowledge, the first example of a nanoscale Kagomé lattice.

The phase is sustained by paramagnetic dicopper(II) tetracarboxylate spin pairs (metal dimers) positioned at the vertices of a Kagomé lattice, and it exploits the concept of self-assembly of nanoscale secondary building units (nSBUs).<sup>[9]</sup> It therefore offers a system where the effect of systematically substituting the molecular components can be evaluated. In this context, we compare the magnetic response of the Kagomé lattice arrangement with a system where identical secondary building units (SBUs)<sup>[10]</sup> are arranged in a tetragonal 2D configuration, which is not expected to exhibit spin frustration.

We have recently demonstrated that regular molecular squares can self-assemble at their vertices to form square or triangular nSBUs, and that the use of an appropriate template and mild crystallization conditions facilitates the generation of a diverse range of discrete and infinite molecular architectures that are based upon these nSBUs.<sup>[9, 11-13]</sup> The ubiquitous dimetal tetracarboxylates  $[\text{M}_2\text{L}_2(\text{O}_2\text{CR})_4]$  ( $\text{L}$  = coordinated ligand,  $\text{M}$  = transition metal) serve as ideal molecular squares in this context since they are synthetically accessible and, depending upon the metal, offer potential as catalysts<sup>[14]</sup> or molecular magnets.<sup>[15, 16]</sup> Figure 1 illustrates the two nSBUs that can be generated if the molecular squares are linked by 1,3-benzenedicarboxylate (bdc), that is, at 120°: a square nSBU (a cluster of four square SBUs) or a triangular nSBU (a cluster of three square SBUs). These nSBUs are known to self-assemble to form discrete nanoballs (sustained by both square and triangular nSBUs)<sup>[12]</sup> or a tetragonal 2D lattice (sustained by square nSBUs only).<sup>[9]</sup> It occurred to us that other supramolecular isomers are possible if triangular nSBUs alone are present: triangular or Kagomé 2D lattices (Figure 2). Few examples of molecular Kagomé lattices have been reported to date,<sup>[17-19]</sup> and to our knowledge there have been no reports of a nanoscale lattice, despite the expectation of cooperative magnetic phenomena in such structures.

Slow diffusion of ethanolic copper(II) nitrate into a solution of bdc, pyridine (py), and an appropriate template (nitrobenzene, 1,2-dichlorobenzene, or naphthalene) in ethanol affords prismatic blue-green crystals of  $[(\text{Cu}_2(\text{py})_2(\text{bdc})_2)_3]_n$  (**1**). The crystal structure of **1**<sup>[20]</sup> (Figure 3) can be described as

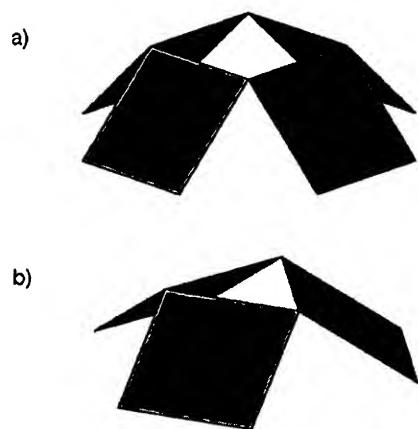


Figure 1. Illustrations of the square (a) and triangular (b) nSBUs that can be formed by linking the vertices of molecular squares.

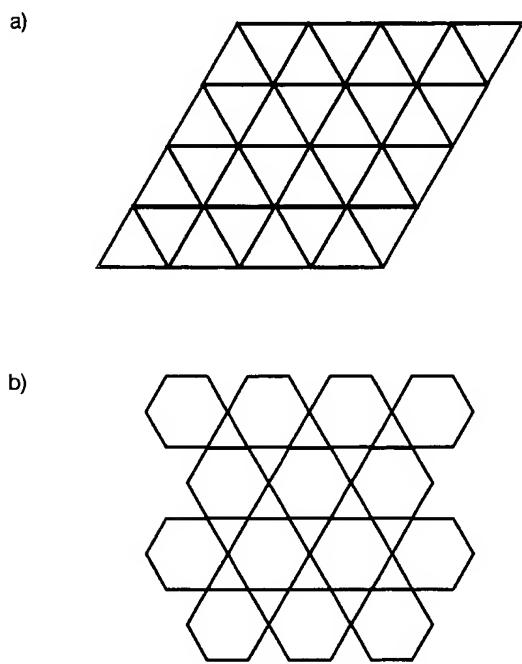


Figure 2. A schematic representation of triangular (a) and Kagomé (b) 2D lattices.

the result of self-assembly of bowl-shaped triangular nSBUs to yield a nanoscale Kagomé lattice. Cu<sub>2</sub> dimers are positioned at the lattice points and are bridged by the bdc ligands, thereby generating large hexagonal cavities within the layer. The bowl-shaped nSBU facilitates efficient packing when the bowls are eclipsed, which results in eclipsing of the hexagonal cavities (0.91 nm effective diameter) and in hexagonal channels of the same dimension. The layers are undulating because of the curvature imparted by the bdc moiety, and have an amplitude of 1.24 nm, with adjacent layers overlapping by approximately 20%. The apical positions of the Cu<sub>2</sub> dimers are occupied by coordinated pyridine ligands, and highly disordered solvent molecules occupy the hexagonal channels (approximately 28% by weight). Thermal analyses

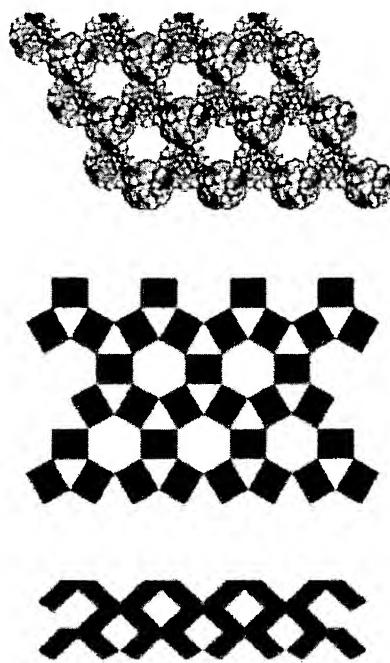


Figure 3. Space-filling and schematic representations of the arrangement of triangular nSBUs in the nanoscale Kagomé lattice structure exhibited by 1.

(thermogravimetric analysis and differential scanning calorimetry) indicate that the solvent of crystallization and the pyridine ligands can be removed at approximately 200°C, and that the desolvated lattice is thermally stable at temperatures in excess of 300°C. The most intense peaks observed in the X-ray powder diffraction patterns from the bulk sample are consistent with those calculated from single-crystal diffraction data. A phase based on square nSBUs,  $\left[\text{((py)}_2\text{Cu}_2(\text{bdc})_2\right]_n$  (2), can be obtained under different crystallization conditions.<sup>[9]</sup>

The magnetic properties of **1** are featured in Figure 4. The temperature-dependent susceptibility ( $\chi$ ) at a constant field ( $H = 0.1$  T) is shown in Figure 4a and the field-dependent magnetization at low temperature ( $T = 5$  K) in Figure 4b. The graphs exhibit rich structure that can be associated with the combined intradimer and interdimer magnetic interactions. Cooperative magnetism in complexes based on Cu<sub>2</sub> dimers has been studied in the past and is known to predominantly exhibit antiferromagnetic coupling.<sup>[21, 22]</sup>

The temperature-dependent  $\chi$  shows a maximum just below 300 K and a minimum at around 60 K followed by an upturn at lower temperature. The data presented have been corrected for the diamagnetic contribution. The variation of  $\chi$  with temperature is consistent with cooperative magnetic behavior observed in dimeric copper complexes. We have used a standard Bleaney–Bowers (BB) model<sup>[23]</sup> to generate a fit to our experimental data, and this is also shown in Figure 4. The two main fit parameters are the intradimer ( $J$ ) and interdimer ( $J'$ ) interaction terms. From our fit, we obtain values of  $J = -350$  and  $J' = -18 \text{ cm}^{-1}$ . Our model also accounts for the presence of uncompensated moments that follow a Curie law.

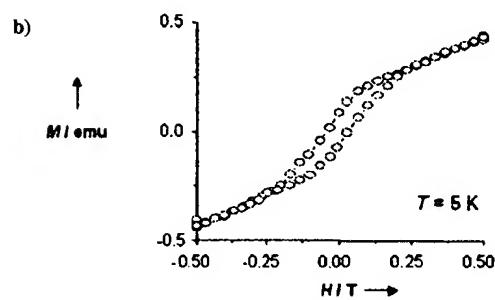
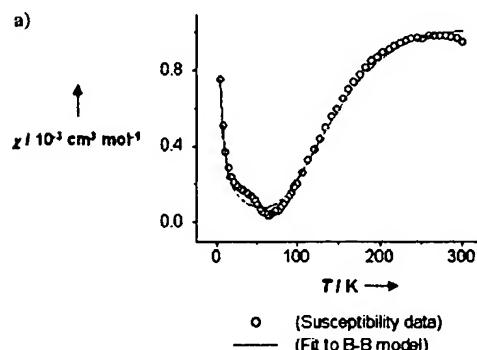


Figure 4. a) The temperature-dependent molar susceptibility ( $\chi$ , per nSBU) of **1** at 0.1 T (data points) overlaid by a plot of the BB best-fit model (solid line);  $J = -350 \text{ cm}^{-1}$  and  $J' = -18 \text{ cm}^{-1}$ ; b) the field-dependent magnetization of **1** at  $T = 5 \text{ K}$ .

This phenomenon is responsible for the upturn in susceptibility at temperatures below 50 K.

A clue as to the nature of the geometrically frustrated antiferromagnetic state inherent in this compound is revealed on investigation of the field-dependent magnetization data, shown in Figure 4b. A well-defined hysteresis loop is observed which is indicative of ferromagnetic behavior. We have also confirmed the presence of hysteresis at 300 K. In a sense, we have demonstrated herein that it is possible to arrange nanoscale molecular objects (not atoms!) with precise control and achieve periodic magnetic nanostructures.<sup>[24]</sup>

Within the context of the triangular Kagomé lattice, we can now attempt to understand the origin of the ferromagnetic-like response leading to magnetic hysteresis. The triangular lattice framework will result in disruption of perfect antiferromagnetic ordering by introducing spin frustration that leads to canted arrangement of spins. Of course, the term "spins" refers here to the moments of the individual dimers. Spin canting can lead to the appearance of effective weak ferromagnetic long-range order. It has also been pointed out that in low-dimensional systems such as semiconductor quantum dots and molecular magnets, electron correlation effects in an antiferromagnetic lattice can lead to flat-band ferromagnetism.<sup>[25]</sup>

Phase **2** exhibits an alternative topology to **1**; the 2D square lattice that is shown in Figure 5. In this case, geometry considerations dictate that spin frustration is ruled out, which is reflected in the magnetic measurements shown in Figure 6. To keep our comparison direct and simple, we have plotted molar susceptibility and magnetization data using identical

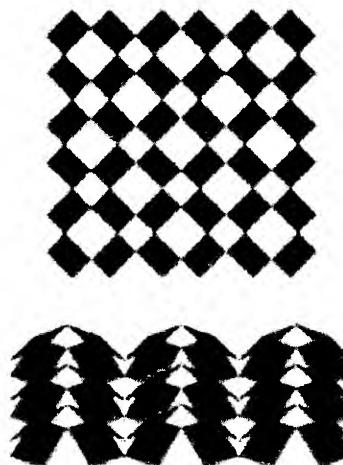
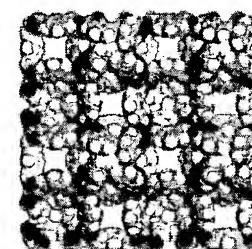


Figure 5. Space-filling and schematic representations of the arrangement of square nSBUs in the nanoscale square lattice structure exhibited by **2**.

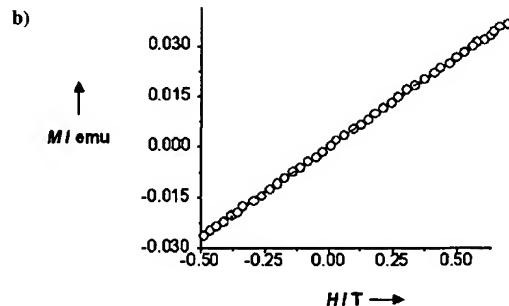
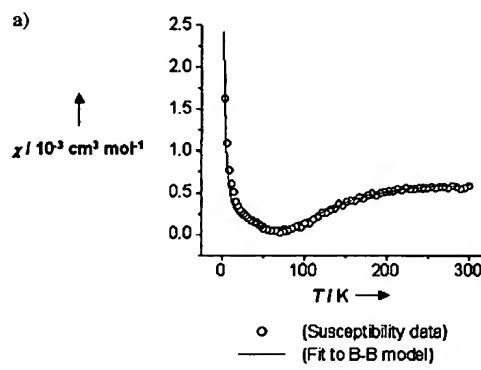


Figure 6. a) The temperature-dependent molar susceptibility ( $\chi$ , per nSBU) of **2** at 0.1 T (data points) overlaid by a plot of the BB best-fit model (solid line);  $J = -380 \text{ cm}^{-1}$  and  $J' = -85 \text{ cm}^{-1}$ ; b) the field-dependent magnetization of **2** at  $T = 5 \text{ K}$ .

## COMMUNICATIONS

conditions to those described in Figure 4. These magnetic data are very similar to recent experimental results reported by other groups on complexes of Cu<sub>2</sub> dimers.<sup>[26]</sup> Theoretical fit using the BB model to the temperature-dependent molar susceptibility data in this case yields fit parameters  $J = -380 \text{ cm}^{-1}$  and  $J' = -85 \text{ cm}^{-1}$ . Clearly, the most striking feature is that the field-dependent magnetization does not display a hysteresis loop in this system, the straight line obtained being representative of a more traditional paramagnetic behavior.

Our results dramatically underscore the potential afforded by supramolecular chemistry for the design of molecular nanostructured assemblies with desirable physical properties, while emphasizing how the composition of a material is not the only feature one must consider when designing a phase that exhibits molecular magnetism. Future work will focus on the modularity of this system and on chemical modification of the components: substituting the metal; changing the coordinated ligand; substituting the bdc ligand; incorporation of different guest molecules. We expect a significant effect on magnetic properties as it has already been shown that simply varying the apical coordinated ligand has a measurable effect on the magnetism exhibited by the SBU used in our study.<sup>[26]</sup>

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channels were modeled as a group of variable-occupancy carbon atoms. CCDC-165791 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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## Substrate Distortion by a $\beta$ -Mannanase: Snapshots of the Michaelis and Covalent-Intermediate Complexes Suggest a $B_{2,5}$ Conformation for the Transition State

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More than 6000 glycosidase sequences and related open reading frames are currently known. They have been classified into some 85 families based upon amino acid sequence similarities<sup>[1]</sup> providing a rich context in which to explore variations in glycosidase mechanism. Experimental demonstration of pyranoside ring conformations along the reaction pathway may assist the design of transition state analogues both as therapeutic agents and mechanistic probes. Here we report the three-dimensional structures of the Michaelis complex and covalent glycosyl–enzyme intermediate for a family-26  $\beta$ -mannanase, both of which display conformational features never previously seen on any glycosidase. When viewed in light of published work on mannosidase inhibition, this work suggests that the transition state for mannoside

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# Hydroxylated nanoballs: synthesis, crystal structure, solubility and crystallization on surfaces

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The reaction of equimolar amounts of  $\text{Cu}(\text{NO}_3)_2$  and bdc-5-OH (bdc-5-OH = benzene-1,3-dicarboxylate-5-hydroxy) affords hydroxylated nanoballs with high solubility and an ability to form microcrystals on surfaces.

The design and generation of nanoscale polyhedral structures via self-assembly represents an approach to synthesis that offers new horizons in the context of synthetic chemistry and its possible impact upon nanotechnology.<sup>1–9</sup> In this context, we have recently reported a design strategy for the one-step synthesis of nanoscale molecules<sup>10</sup> and frameworks<sup>11,12</sup> that are based upon self-assembly of structure building units (SBUs),<sup>13</sup>  $\text{M}_2(\text{O}_2\text{CR})_4$  molecular squares, at their vertices. The discrete structures, which we have termed ‘nanoballs’, are molecular versions of faceted polyhedra,<sup>14</sup> namely small rhombihexahedra, and are depicted schematically in Fig. 1. The key to obtaining ‘nanoballs’ cleanly and in high yield is that the square SBUs are linked at a  $120^\circ$  angle using the angular bifunctional ligand benzene-1,3-dicarboxylate, bdc. They are distinguished by their nanoscale size, their facile synthesis and the potential for functionalisation at multiple sites: the inner or outer metal centres, the interior cavity, or the bridging ligand. In this contribution we report the first example of a small rhombihexahedron that is functionalised at the bridging ligand, bdc-5-OH serving as the ligand.

The small rhombihexahedron  $[(\text{DMSO})(\text{MeOH})\text{Cu}_2(\text{bdc}-5\text{-OH})_2]_{12}$ , **1**, formed spontaneously upon the addition of 2,6-dimethylpyridine (2 equivalents) to a methanolic solution of  $\text{Cu}(\text{NO}_3)_2$  (1 equivalent) and  $\text{H}_2\text{bdc-5-OH}$  (1 equivalent). Addition of diethyl ether precipitated a crude product, re-crystallization of which from DMSO afforded single crystals of **1** suitable for X-ray crystallography.<sup>†</sup> The crystal structure of **1** is illustrated in Fig. 2. **1** has DMSO ligands axially bonded to the metal ions that lie at the exterior surface of the nanoball, and MeOH ligands axially bonded to the metal ions that lie at the interior surface of the ball. It has a molecular volume, including solvent sphere,  $> 17 \text{ nm}^3$  and a molecular weight of 7.43 kDa. The internal cavity has a volume of ca.  $1 \text{ nm}^3$ . Crystals of **1** appear to be stable indefinitely if in contact with the mother-liquor but are highly deliquescent if removed from mother-liquor.

The presence of 24 hydroxy groups on the surface of the nanoball predictably alters the chemical and physical properties

when compared to the unsubstituted analogues. For example, **1** is readily soluble in a variety of organic solvents, including methanol, ethanol, iso-propyl alcohol, DMF and hot acetonitrile. This has allowed us to grow microcrystals of **1** on mica or glass, *via* evaporation of methanol solutions of **1**.

Atomic force microscopy (AFM) has become one of the most widely used tools for the study of crystal growth and behaviour on surfaces,<sup>15–20</sup> examples include size control of nano-crystals on Langmuir–Blodgett films,<sup>15</sup> protein crystal growth,<sup>16</sup> molecular and nanotribology,<sup>17</sup> statistical analysis of 2-D crystal sizes,<sup>18</sup> dopant effects on crystal growth<sup>19</sup> and annealing effects on crystallisation.<sup>20</sup> AFM studies<sup>‡</sup> revealed that the micro-crystals of **1** are of quite uniform dimensions and that they are stable even after mild heating.

The images obtained on a mica surface, without thermal treatment, show increasing density of microcrystals with increasing concentration. The microcrystals have an average height of 140 nm with a variation of 30 nm; the roughness (RMS) is 56 nm. The average size is 1.3  $\mu\text{m}$  with a variation of 0.4  $\mu\text{m}$ . In the case of the films prepared on glass, observation on samples not thermally treated gave poor image quality even in the non-contact mode due to the presence of residual solvent forming a strongly bound contamination film. This contamination layer can be removed by heating to 37 or 75 °C during 24 h. The corresponding images are shown in Fig. 3(a) and (b), respectively; the roughness (RMS) is 236 nm and 261 nm. Image analysis shows an average size of 1.4  $\mu\text{m}$  for the sample annealed at 37 °C and again 1.4  $\mu\text{m}$  for that annealed at 75 °C, the variance is 0.4  $\mu\text{m}$ . It is interesting that there is no apparent difference in the crystal sizes either on different substrates or under different thermal treatment. The average heights are 500 and 600 nm, respectively. For the sample treated at 37 °C the height values are randomly distributed about this average. However, for the sample treated at 75 °C there is a clear statistical distribution of heights at 300, 600 and 900 nm. Whilst it is apparent that annealing at higher temperature leads to a higher density of crystals, it is of interest that there is apparently non-crystalline material present between the microcrystals in Fig. 3(a). This situation is analogous to that observed for thermally treated thin films of *tert*-butylcalix[4]arene.<sup>21</sup> It would appear that annealing at the higher temperature gives rise

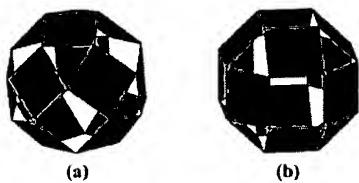


Fig. 1 Schematic representations of the small rhombihexahedra that exist for  $[(\text{MeOH})_2\text{Cu}_2(\text{bdc})_2]_{12}$ , **a**, and  $[(\text{Py})(\text{MeOH})\text{Cu}_2(\text{bdc})_2]_{12}$ , **b**. The two polyhedra differ in the connectivity of the SBUs.

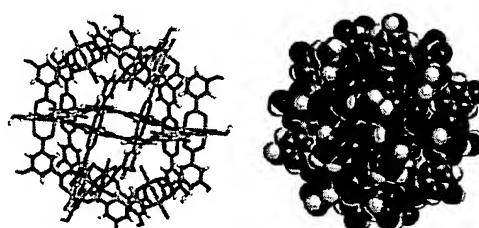
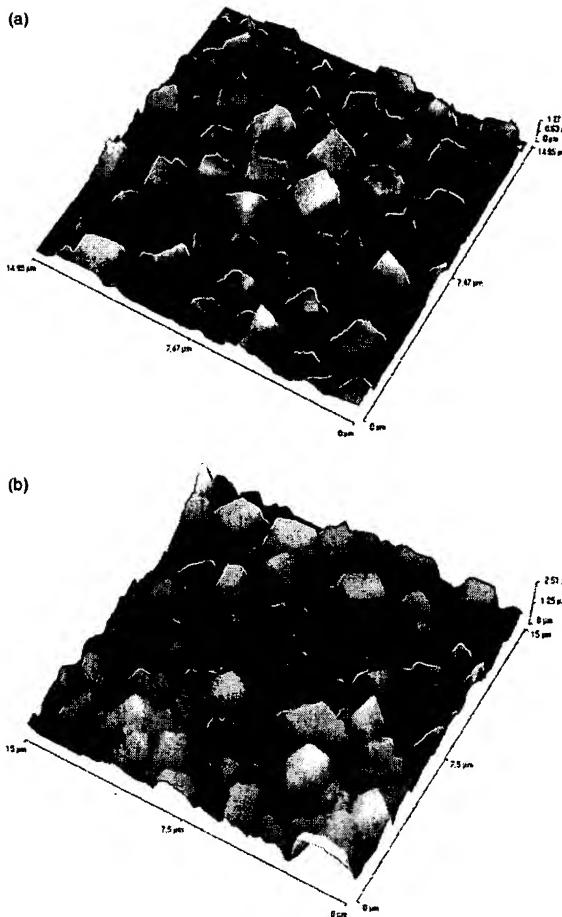


Fig. 2 Crystal structure of  $[(\text{DMSO})(\text{MeOH})\text{Cu}_2(\text{bdc}-5\text{-OH})_2]_{12}$  **1**. The connectivity of the SBUs in **1** is the same as in **b**.



**Fig. 3** (a) Non-contact mode AFM image of microcrystals of **1** on glass after annealing at 37 °C for 24 h. (b) Non-contact mode AFM image of microcrystals of **1** on glass after annealing at 75 °C for 24 h.

to a complete crystallisation of the film and that there is a definite self-organisation producing structures for which the heights are multiples of 300 nm. The existence of nanoscale channels in the crystal structure of **1** is a consequence of the inability of spheres to close-pack efficiently and the inherent open structure that must occur for a faceted polyhedron. We are therefore evaluating **1** for possible use in sensors.

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#### Notes and references

† *Crystallographic data:* intensity data for **1** were collected at 200 K on a Bruker SMART-APEX diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.7107$

Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structure was solved using direct methods and refined by full-matrix least-squares on  $|F|^2$ . All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. The calculated density is very low and a reflection of the large amounts of space in the unit cell that are occupied by disordered solvent molecules.

*Crystal data for **1**:* tetragonal, space group  $I4/mmm$ ,  $a = b = 31.111(4)$ ,  $c = 35.999(6)$  Å,  $V = 34844(8)$  Å $^3$ ,  $Z = 2$ ,  $D_c = 0.708$  g cm $^{-3}$ ,  $\mu = 0.778$  mm $^{-1}$ ,  $F(000) = 7366$ ,  $2\theta_{\max} = 42.08^\circ$  ( $-30 \leq h \leq 31$ ,  $-31 \leq k \leq 31$ ,  $-36 \leq l \leq 21$ ). Final residuals (for 296 parameters) were  $R_1 = 0.1531$  for 5170 reflections with  $I > 2\sigma(I)$ , and  $R_1 = 0.2128$ ,  $wR_2 = 0.4702$ ,  $GOF = 1.679$  for all 49928 data. Residual electron density was 1.051 and  $-0.592$  e Å $^{-3}$ .

CCDC reference number 169279. See <http://www.rsc.org/suppldata/cc/b1/b106592k/> for crystallographic data in CIF or other electronic format.

‡ *Atomic force microscopy data:* films of **1** were prepared by deposition of 20 μL of a solution of **1** in methanol, at varying concentrations, onto either freshly cleaved mica or freshly cleaned glass slides. Images of deposited films of **1** on mica or glass were collected using a Thermomicroscopes Explorer AFM. Scan sizes from 80 to 5 μm were collected in amplitude detection in the non-contact mode. Cantilevers were HRF with a resonance frequency of 270 kHz, scan rates were 1 Hz. Image resolution was 500 × 500. Images are unfiltered.

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- [6] Crystal data for **1**·hexane: colorless crystal,  $0.18 \times 0.23 \times 0.38$  mm, triclinic,  $P\bar{1}$ ,  $a = 10.7828(3)$ ,  $b = 13.1998(5)$ ,  $c = 16.1826(7)$  Å,  $\alpha = 105.724(2)$ ,  $\beta = 103.774(2)$ ,  $\gamma = 92.199(3)^\circ$ ,  $V = 2140.2(7)$  Å $^3$ ,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.098$  g cm $^{-3}$ ,  $\mu = 0.120$  mm $^{-1}$ ,  $2\theta_{\text{max}} = 56.5^\circ$ . A total of 10232 ( $R_{\text{int}} = 0.053$ ) unique reflections were collected (Enraf Nonius CCD, Mo $K\alpha$  radiation ( $\lambda_0 = 0.71073$  Å),  $T = 123$  K) and used in least-squares refinement on  $F^2$ , 469 refined parameters, GOF = 1.030 (based on  $F^2$ ),  $R_1 = 0.073$ ,  $\omega R_2 = 0.169$  ( $I > 2\sigma(I)$ ),  $R_1 = 0.134$ ,  $\omega R_2 = 0.198$  (all data), residual electron density = -0.366/0.525 e Å $^{-3}$ . The hydrogen atoms were placed in calculated positions using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157276. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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- [13] Typical elemental analyses calcd for **1** C<sub>72</sub>H<sub>98</sub>Li<sub>10</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>4</sub> (%): C 65.06, H 7.43, N 4.21 (1·hexane C<sub>78</sub>H<sub>112</sub>Li<sub>10</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>4</sub>: C 66.19, H 7.98, N 3.96); found: C 62.98, H 7.74, N 4.44.

## Self-Assembly of Nanometer-Scale Secondary Building Units into an Undulating Two-Dimensional Network with Two Types of Hydrophobic Cavity\*\*

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By using some of the recently enunciated principles of crystal engineering<sup>[1-3]</sup> and self-assembly it has become possible to design and construct new classes of crystalline compounds from molecular components that possess useful

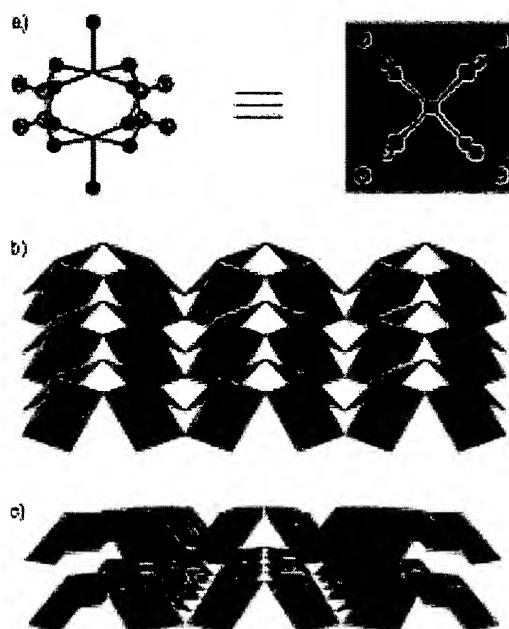
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physical properties including bulk magnetism,<sup>[4]</sup> nonlinear optical properties,<sup>[5]</sup> and porosity.<sup>[6-9]</sup> Open-framework structures can be assembled by using metals or metal clusters as nodes and multifunctional organic ligands to link these nodes. This approach has afforded structures that exhibit high surface areas, affinity for a wide range of organic guest molecules,<sup>[10]</sup> and some show potential for catalysis.<sup>[9]</sup> Herein we illustrate how the use of metal-organic secondary building units (SBUs) that are linked by angular ligands can generate nanoscale SBUs (nSBUs) with curvature.

The use of carboxylate-bridged metal clusters as metal-organic SBUs to build extended self-assembled structures has been delineated by Yaghi et al.<sup>[8]</sup> Scheme 1a illustrates such a



Scheme 1. Schematic illustrations of a) the square SBU (green) based on metal ions bridged by carboxylate anions, b) how the square SBUs can self-assemble at their vertices to generate nanosized bowls (purple) which in turn form curved sheets, and c) how the curved sheets pack because of shape considerations.

cluster—in this case two metal ions are bridged by four carboxylate anions and each metal is bonded to one axial pyridine ligand. When viewed along the axial direction the extension of the carboxylate ligands forms a “square SBU”. Such clusters are ubiquitous in the Cambridge Structural Database,<sup>[11]</sup> but most contain monofunctional carboxylates and, therefore, they will not generate extended structures. However, the use of bifunctional carboxylate ligands such as 1,4-benzenedicarboxylate allows the formation of self-assembled infinite structures that contain channels capable of incorporating a variety of guest molecules.<sup>[12-15]</sup> 1,3-Benzene-dicarboxylate is suitable for the linking of square SBUs at 120° and Scheme 1b shows one of the ways in which square SBUs can pack when there is a 120° angle at their vertices: a two-dimensional (2D) infinite metal-organic framework resembling a layer of upended bowls. In such a structure one bowl

may be regarded as a “nanometer-scale SBU” (nSBU) which consists of four metal cluster SBUs.

The compounds  $\{[M_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n$  (**1**) ( $1,3\text{-bdc}$  = 1,3-benzenedicarboxylate, py = pyridine, M = Zn, **1a**, Cu, **1b**) demonstrate that four square SBUs can indeed combine to form one bowl-shaped nSBU ( $\{[M_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n$ ), which in turn self-assembles with other nSBUs to form the undulating sheet structure depicted in Scheme 1b. Each bowl has an outer diameter of 0.94 nm; a depth (as measured by the perpendicular distance from the center of the base to midpoint of a line joining the top hydrogen atoms on opposite bdc moieties) of 0.84 nm and a solvent-accessible volume of  $0.518 \text{ nm}^3$ .<sup>[16]</sup> The bowls are occupied by disordered benzene or pyridine guests and by the bottom of a bowl from the adjacent sheet. The layers therefore pack as illustrated in Scheme 1c, giving rise to a channel between adjacent bowls. The channels are hour-glass-shaped with a cavity of maximum dimensions of about  $0.90 \times 0.90 \times 0.65 \text{ nm}$  and are occupied by benzene or pyridine guest molecules (in one unit cell the solvent-accessible volume is  $0.28 \text{ nm}^3$ ). Between these cavities the channel narrows to an opening of about  $0.15 \times 0.15 \text{ nm}$  which restricts the movement of the guest molecules through the channel. The distance between guest molecules is 0.81 nm. Figure 1a presents the coordination networks, and Figure 1b illustrates the networks in stick representation and the guest molecules in the channel in space-filling mode (the guests in the bowls have been omitted for clarity). The profile of the hour-glass channel is shown in Figure 1c. The total volume of both types of cavity represents about 23% of the volume of the unit cell.<sup>[17]</sup> Single crystals maintained at room temperature under vacuum overnight gave identical thermogravimetry MS curves to those obtained directly from solution, indicating that **1** is stable at ambient temperatures. However, thermogravimetry data also indicates that crystals of **1** are not stable to loss of guest because the pyridine ligands must be removed from the metal cluster to facilitate free release of guest molecules.

In summary, **1a** and **1b** exhibit an infinite 2D structure formed by the self-assembly of nSBUs that are formed by four square carboxylate-bridged di-metal(*ii*) SBUs. Compounds **1a** and **1b** are curved as a result of the  $120^\circ$  angle subtended by the bdc ligands and that they may be considered to be supramolecular isomers<sup>[18]</sup> of discrete polyhedra based upon molecular squares. The shape and chemical nature of the bowls in **1** resembles calixarenes and we are investigating the ability to incorporate guest molecules that are known to form complexes with calixarenes.<sup>[19]</sup>

#### Experimental Section

$\{[Zn_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n \cdot \text{benzene/pyridine}$  (**1a**): A methanolic solution (20 mL) of  $Zn(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1 mmol, 0.297 g) and benzene-1,3-dicarboxylic acid (1 mmol, 0.166 g) in the presence of pyridine (0.5 mL) and benzene (1 mL) was refluxed for about 30 mins. Slow cooling at room temperature afforded colorless crystalline plates of **1a**.

$\{[Cu_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n$  (**1b**): An ethanolic (10 mL) solution containing lutidine (0.90 mmol, 0.1 mL) was layered onto  $Cu\text{NO}_3 \cdot 2.5\text{H}_2\text{O}$  (0.231 g, 1.0 mmol) and benzene-1,3-dicarboxylic acid (0.360 g, 2.2 mmol) in DMF (10 mL). Slow diffusion over several days yielded blue platelike crystals of **1b**. Single crystals of **1a** and **1b** were subjected to thermogravimetry–mass spectrometry (TG-MS) analysis on a TA Instruments 2950 TGA with  $N_2$  as

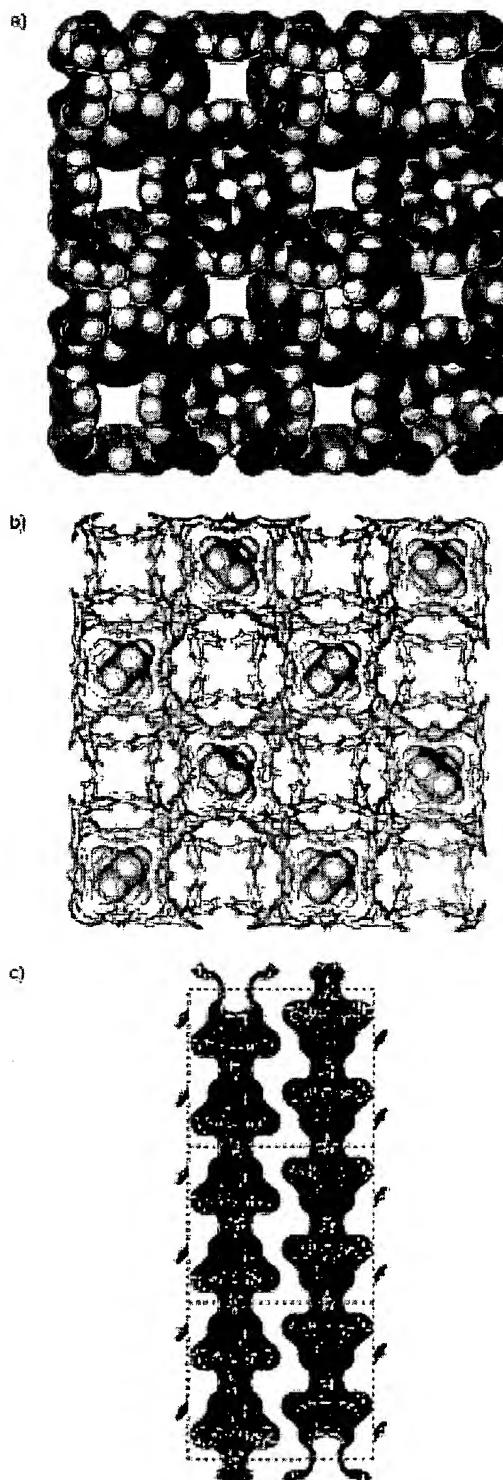


Figure 1. a) Space-filling diagram of the crystal structure of  $\{[M_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n$ . Guest molecules have been omitted for clarity. b) Structure of  $\{[M_2(1,3\text{-bdc})_2(\text{py})_2]_4\}_n$ , viewed along [001]. The guest molecules occupying the hour-glass channels are shown with van der Waals radii. Each bowl is also occupied by a benzene or pyridine guest, which has been omitted for clarity. c) Profile of the hour-glass shaped channels between adjacent bowls. The shaded area is the empty volume; guest molecules are located in the widest areas of the channels.

purge gas. The crystals are thermally stable to above 150°C after which the TG curve shows a mass loss of about 33 % between 180 and 300°C, which is consistent with and corresponds to the loss of benzene ( $M^+ = 78$ ) and pyridine ( $M^+ = 79$ ). Further heating leads to decomposition above 400°C. The IR spectrum shows two strong peaks at 1635 cm<sup>-1</sup> and 1446 cm<sup>-1</sup>; the difference between these peaks is 189 cm<sup>-1</sup> as would be expected for bridging bidentate carboxylates.<sup>[20]</sup>

Crystal data for **1a**: Tetragonal,  $P4/ncc$ ,  $a = 19.0356(9)$ ,  $c = 16.253(1)$  Å,  $V = 5889.3(6)$  Å<sup>3</sup>,  $Z = 8$  (for  $[\text{Zn}_2(1,3\text{-bdc})_2(\text{py})_2]$ ),  $\rho_{\text{calcd}} = 1.744$  g cm<sup>-3</sup>,  $\mu = 1.69$  mm<sup>-1</sup>,  $F(000) = 3168$ ,  $2\theta_{\text{max}} = 50.1^\circ$ . Crystal data for **1b**: Tetragonal,  $P4/ncc$ ,  $a = 18.7912(8)$ ,  $c = 16.8886(10)$  Å,  $V = 5963.5(8)$  Å<sup>3</sup>,  $Z = 8$  (for  $[\text{Cu}_2(1,3\text{-bdc})_2(\text{py})_2]$ ),  $\rho_{\text{calcd}} = 1.507$  g cm<sup>-3</sup>,  $\mu = 1.48$  mm<sup>-1</sup>,  $F(000) = 2750$ ,  $2\theta_{\text{max}} = 56.54^\circ$ . The data for **1a** and **1b** were collected at -100°C on a Bruker SMART APEX diffractometer using Mo $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å) and were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$ .<sup>[21]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the pyridine and bdc ligands were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their parent atoms. The guest molecules inside the bowl-shaped cavity were disordered in such manner that they could not be readily resolved. Guest molecules in the hour-glass-shaped channels were better resolved, but it is not possible to differentiate between benzene and pyridine molecules in these channels. Guest atoms were therefore treated as carbon atoms and refined with fixed isotropic thermal parameters and variable site occupancy. Final residuals for **1a** were  $R1 = 0.0372$  and  $wR2 = 0.0958$  for 1782 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.0591$ ,  $wR2 = 0.1028$  for all 2625 data (181 parameters). Values for **1b** were  $R1 = 0.0407$  and  $wR2 = 0.1063$  for 2289 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.0680$ ,  $wR2 = 0.1139$  for all 3632 data. Residual electron density was 0.82 and -0.58 e Å<sup>-3</sup> for **1a** and 0.96 and -0.87 e Å<sup>-3</sup> for **1b**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152547 and CCDC-162957. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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## Polygons and Faceted Polyhedra and Nanoporous Networks\*\*

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Design principles that are based upon the concepts of crystal engineering and self-assembly have recently afforded new classes of crystalline solids that possess important physical properties such as bulk magnetism<sup>[1, 2]</sup> or porosity.<sup>[3–5]</sup> Furthermore, given that these structures are designed from first principles, they offer chemists an inherent ability to control the chemical nature of the molecular components and therefore influence the bulk physical properties of the material. Similar principles of self-assembly have been applied toward the design and isolation of nanosized spheroid architectures that are based upon regular (Platonic) and semiregular (Archimedean) polyhedral solids.<sup>[6–13]</sup> However, there exist other well-documented examples of uniform polyhedra<sup>[14, 15]</sup> that to our knowledge remain unexplored at the molecular level. In particular, there are nine polyhedra that are closely related to Platonic and Archimedean solids but differ in that they can be designed and built through linking of the vertices of polygons rather than the edges of polygons. Such structures are termed *faceted polyhedra*<sup>[16]</sup> (Figure 1a) since they necessarily contain both open and closed faces. Of particular interest in the context of this study are those polyhedra that are sustained by triangles, squares, or combinations thereof.

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*Communications***Suprasupermolecular Chemistry: Infinite Networks from Nanoscale Metal–Organic Building Blocks<sup>†</sup>**

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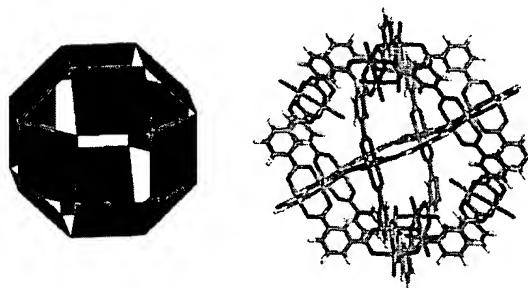
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**ABSTRACT:** Nanoball structures decorated by 24 sulfonate or 24 methoxy moieties, **1** and **2**, respectively, are able to act as nodes for the generation of infinite networks.

Self-assembly of preselected molecular components for the purpose of supramolecular synthesis<sup>1–3</sup> represents the underpinning for two topical areas of synthetic and structural chemistry: “bottom-up”<sup>4</sup> one-pot generation of discrete nanoscale molecular structures and crystal engineering of crystalline solids with novel compositions and topologies.<sup>5</sup> In the case of the former, metal–organic,<sup>6</sup> organic,<sup>7</sup> and inorganic<sup>8</sup> structures of hitherto unprecedented scale have been isolated via design principles that invoke geometric as well as chemical considerations to generate curvature and enclose space. Crystal engineering invokes similar design principles, but molecular components are preselected for their ability to facilitate the generation of infinite rather than closed structures, typically via a “node and spacer” approach. It is perhaps surprising that only recently has it been demonstrated that these two areas can overlap with the confirmation that certain discrete nanoscale structures can serve as nodes in the formation of infinite networks.<sup>9</sup>

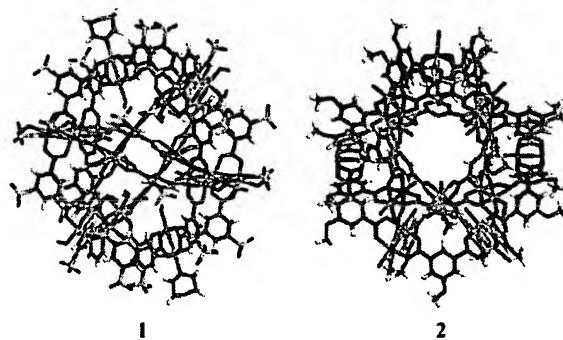
A molecular component that has served as a molecular building block for both discrete and infinite structures is 1,3-benzenedicarboxylic acid, H<sub>2</sub>bdc, which has been exploited for the generation of compounds of formula [Cu<sub>2</sub>(bdc)<sub>2</sub>L<sub>2</sub>]<sub>n</sub> (L = pyridine, substituted pyridine, MeOH; n = 12).<sup>10,11</sup> The nanoscale molecular *small rhombihexahedra* of formula [Cu<sub>2</sub>(bdc)<sub>2</sub>L<sub>2</sub>]<sub>12</sub>, illustrated in Figure 1, can be regarded as being a self-assembly of vertex-linked dicopper tetracarboxylate<sup>12</sup> squares for which bdc is ideally suited since it subtends the required 120° angle. These metal–organic nanoballs appear ideally suited for exploitation as nanoscale building blocks because they are predisposed toward further decoration at either the axial metal sites or the bdc ligand. In this contribution, we address decoration of the prototypal nanoball and how it thereby becomes feasible to engage in a form of suprasupermolecular chemistry.<sup>13</sup>



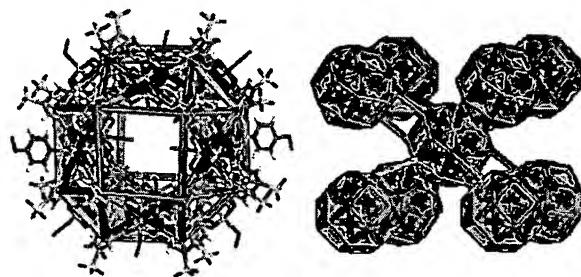
**Figure 1.** Schematic and cylinder representations of the neutral small rhombihexahedron of formula [Cu<sub>2</sub>(bdc)<sub>2</sub>L<sub>2</sub>]<sub>12</sub>.

Crystals<sup>14</sup> of sulfonated anionic nanoballs, {[Cu<sub>2</sub>(5-SO<sub>3</sub>-bdc)<sub>2</sub>(4-methoxypyridine)<sub>0.50</sub>(MeOH)<sub>x</sub>(H<sub>2</sub>O)<sub>1.50-x</sub>]<sub>12</sub>}<sup>24-</sup>, **1**, result from modular self-assembly in MeOH under ambient conditions<sup>15</sup> of 72 molecular components: 24 5-SO<sub>3</sub>-bdc moieties, 24 Cu(II) cations, 18 coordinated solvent (MeOH/H<sub>2</sub>O), and 6 coordinated base (4-methoxypyridine) molecules. The molecular mass of each anion is ca. 8.6 kDa and their molecular volume is ca. 24.4 nm<sup>3</sup>. Importantly, all 24 sulfonate moieties are exposed at the exterior of the nanoball, which is pseudooctahedral in symmetry. They are therefore predisposed for coordination to Cu(II), and, in the presence of excess copper (II) nitrate, 16 sulfonate moieties bond to 16 [Cu(methoxypyridine)<sub>4</sub>]<sup>2+</sup> cations that facilitate cross-linking via axial coordination to a second sulfonate moiety that lies on an adjacent nanoball. The Cu–N distances in the bridging CuN<sub>4</sub>O<sub>2</sub> moieties fall within an expected range (1.98–2.07 Å). However, whereas the Cu–O distances of the CuN<sub>4</sub>O<sub>2</sub> moieties which cross-link the nanoballs along the xz plane are within a narrow range (2.38–2.41 Å), the Cu–O distances of the remaining eight cross-linking moieties vary significantly (2.33–2.85 Å). This variation is consistent with what would be expected for this chromophore.<sup>16</sup> Figure 3 presents a schematic illustration of a single nanoball of **1** and its crystal packing, which is necessarily bcc because of the symmetry of **1** and the nature of the cross-linking (pairs of [Cu(methoxypyridine)<sub>4</sub>]<sup>2+</sup>

<sup>†</sup> CCDC 224752 and 224753 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).



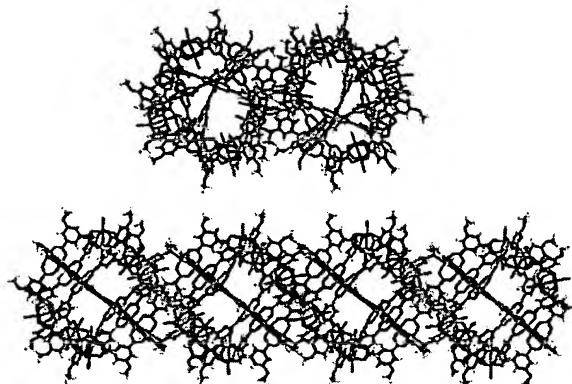
**Figure 2.** Crystal structures of the two decorated nanoballs reported herein: **1** and **2**. **1** is an anion with a 24- charge, whereas **2** is neutral. Outer dimensions of the nanoballs (measured from opposite groups at the periphery) are 3.6 and 2.8 nm, respectively. The inner cavity has a volume of ca. 1 nm<sup>3</sup>, but it is occupied by 12 solvent molecules that are coordinated to the inner axial coordination sites.



**Figure 3.** Schematic model of **1** and its crystal packing which is sustained by double cross-linking. Solvent molecules, interstitial 4-methoxypyridinium cations, and Cu[(4-methoxypyridine)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> are omitted for the sake of clarity.

cations cross-link to the same nanoball). The distance from the center of each nanoball to adjacent nanoballs averages 3.05 nm, and each nanoball sits around a crystallographic inversion center. Distances and angles within **1** are statistically identical to those observed in the prototypical nanoball (Cu-carboxylate and Cu-Cu distances average 1.96 and 2.64 Å, respectively). The net negative charge of the network is balanced by two [Cu(methoxypyridine)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> cations and 4-methoxypyridinium cations that are located in interstitial spaces.

Crystals<sup>14,15</sup> of methoxylated, neutral nanoballs of formula [Cu<sub>2</sub>(5-MeO-bdc)<sub>2</sub>(MeOH)<sub>x</sub>(H<sub>2</sub>O)<sub>1.83-x</sub>]<sub>12</sub>, **2**, result from the modular self-assembly in MeOH under ambient conditions of 70 molecular components: 24 5-MeO-bdc moieties, 24 Cu(II) cations (from copper (II) nitrate), and 22 coordinated solvent (MeOH or H<sub>2</sub>O) molecules. The molecular mass of each molecule is ca. 6.9 kDa and their molecular volume is ca. 11.5 nm<sup>3</sup>. **2** exists as a structural isomer of a *small rhombihexahedron* in which the connectivity of square moieties is slightly different.<sup>10a</sup> The 24 methoxy moieties are disposed at the exterior of the nanoball, and they are capable of coordinating to metal centers through their ether oxygen atoms. Indeed, two methoxy moieties on each nanoball coordinate to axial sites on adjacent nanoballs in such a way that double cross-linking occurs. As revealed in Figure 4, this cross-linking also occurs at the opposite face of each nanoball, thereby generating an infinite 1D chain of nanoballs. The Cu-O distances, averaging 2.26 Å, are consistent with expected values and the separation between centers of adjacent nanoballs is 2.15 nm. The manner in which the 1D chains pack can be described as *hexagonal packing of parallel cylinders (rods)*.<sup>17</sup> It should be noted that because **2** self-assembles through



**Figure 4.** Illustrations of the connectivity between nanoballs in **2**. The upper diagram presents the methoxy moieties that bridge adjacent nanoballs in green. The resulting superstructure is that of a 1D chain sustained by these cross-links. Solvent molecules omitted for clarity.

interaction between axial metal sites on one nanoball and substituted bdc ligands on another nanoball it represents an example of a self-assembled structure that is obtained from a single nanoscale building block. However, complementary moieties, a nanoball and a monometallic chromophore, generate the network structure observed in compound **1**.

In summary, herein we present confirmation that nanoballs of formula [Cu<sub>2</sub>(bdc)<sub>2</sub>L<sub>2</sub>]<sub>n</sub> can be generated with exterior functionality that in turn facilitates crystal engineering of 3D and 1D network structures that contain nanoballs as nodes. Our results suggest that metal-organic nanoballs will exhibit a rich suprasupramolecular chemistry via either single component self-assembly or multiple component (modular) self-assembly.

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- (15) A methanol solution of 5-sulfoisophthalic acid sodium salt (135 mg, 0.503 mmol) and Cu(II) nitrate hemipentahydrate (115 mg, 0.494 mmol) was layered on top of a methanolic solution of 4-methoxypyridine (0.15 mL, 1.5 mmol) and nitrobenzene (2.0 mL). Blue-green crystals of **1** were harvested after 1 day (32 mg, 17%). Green crystals of **2** were formed by layering a methanolic solution of 5-methoxyisophthalic acid (20 mg, 0.10 mmol) and 2,6-lutidine (0.035 mL, 0.30 mmol) onto a methanol/nitrobenzene solution of  $Cu(NO_3)_2 \cdot 2.5H_2O$  (23 mg, 0.099 mmol).
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CG034199D

## A molecular sphere of octahedral symmetry†

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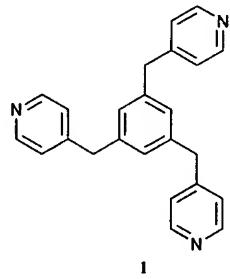
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Complexation of tridentate ligand **1** with  $\text{Pd}(\text{NO}_3)_2$  leads to the quantitative self-assembly of  $\text{M}_6\text{L}_8$  molecular sphere **2**.

Synthesis of molecular architectures from organic ligands and transition metal ions through the self-assembly route, in contrast to the troublesome stepwise synthesis, has received much attention during the last decade.<sup>1</sup> Designed structures having predetermined structural and functional properties can sometimes be obtained by simply mixing the participating components under suitable conditions. Recently, the focus of several groups has been on the construction of self-assembled species possessing internal cavities.<sup>2,3</sup> There are handful of structures with a 3-D cavity within a tetrahedron,<sup>4</sup> hexahedron,<sup>5</sup> dodecahedron,<sup>6</sup> and similar shapes,<sup>7</sup> obtained by a metal-directed self-assembly route. There are also reports of 3-D cavities constructed by utilizing the principle of hydrogen-bond interactions.<sup>8</sup> Secondary building units, the metal ion containing self-assembled structures possessing lateral sites capable of H-bonding interactions, are used successfully to construct cuboctahedron and faceted polyhedra.<sup>9</sup> However, not many reports are available on closed cavities which are more or less spherical in shape although the formation of discrete spherical structures through self-assembly process exists in some biological systems: e.g., the capsids of bacteriophages P22<sup>10</sup> or HK97.<sup>11</sup>

Herein, we report the self-assembly of a novel and highly symmetrical molecular sphere and its X-ray crystal structure. The molecular sphere is constructed from ligand **1**<sup>12</sup> and  $\text{Pd}(\text{NO}_3)_2$ . The complexation reaction was also monitored by using NMR spectroscopy that establishes a quantitative self-assembly process. The findings show reliable evidence of both solution and solid-state structures. The spherical shape is important because the cavity volume is maximized when the components are oriented spherically. Very recently, Liu and Tong reported an  $\text{M}_6\text{L}_8$  assembly which is topologically the same as our molecule but not spherical.<sup>13</sup>



The surface of a sphere is divided by three orthogonal planes into eight identical parts, each of which is capped by the tripodal tridentate ligand **1** (Fig. 1). At each of the six cross sections, one  $\text{Pd}^{(II)}$  ion is located and four ligand molecules are assembled



Fig. 1 Cartoon representation of a molecular sphere, conceptualized from eight tripodal tridentate ligands, and six metal ions that can provide a square planar coordination environment. All the 14 components are cooperatively embracing the surface of sphere.

around the square planar coordination environment of the metal center. Thus, we used  $\text{Pd}(\text{NO}_3)_2$  in combination with **1** in expectation of an aesthetically pleasing  $\text{M}_6\text{L}_8$  type complex. The ligand **1** was mixed with  $\text{Pd}(\text{NO}_3)_2$  at a ratio of 4:3 in DMSO (concentration of **1** = 10 mM), and stirred at 90 °C for 1 h. Subsequent addition of acetone to the above solution precipitated a cream colored solid which was separated by filtration, washed with MeOH, and dried *in vacuo* to obtain hexanuclear complex  $[(\text{Pd})_6(\text{L})_8(\text{NO}_3)_{12}]$  (**2**) in 79% yield.‡

NMR and CSI-MS analyses indicated the formation of predetermined, discrete species **2** by the metal-driven route. In  $^1\text{H}$  NMR, down field shifting of the signals for complex **2** (Fig. 2), particularly for  $\text{Py}_\alpha$  ( $\Delta\delta = 0.69$  ppm), can be ascribed to the metal-ligand complexation. A simple pattern of the spectrum suggested the formation of a highly symmetric discrete species. Complex **2** was also characterized by  $^{13}\text{C}$  NMR spectroscopy.

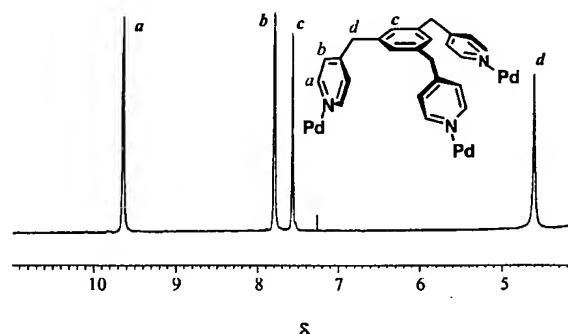


Fig. 2  $^1\text{H}$  NMR spectrum of sphere **2** (500 MHz,  $\text{DMSO-d}_6$ , 25 °C, TMS as an external standard). A partial structure of **2** is shown for convenience. Down field shifting of the signal as compared to free ligand **1**:  $\Delta\delta = 0.69$ , 0.08, 0.05 and 0.19 ppm for  $\text{H}_\alpha$ ,  $\text{H}_\beta$ ,  $\text{H}_\gamma$  and  $\text{H}_\delta$ , respectively.

Peaks in the proton and carbon NMR spectra were completely assigned using H–H COSY, C–H COSY and DEPT techniques. These spectroscopic evidences suggest that all the eight ligands involved in the structure are disposed in the same environment and four-fold symmetry axes pass through the axially located metal centers. The peaks observed in CSI–MS at  $m/z$  1335, 985, 776, and 701 corresponding to  $[2 - (\text{NO}_3)_3]^{3+}$ ,  $[2 - (\text{NO}_3)_4]^{4+}$ ,  $[2 - (\text{NO}_3)_5]^{5+}$ , and  $[(2 - (\text{NO}_3)_6) + 5\text{DMSO}]^{6+}$  strongly support the formation of the assumed structure. Elemental analysis of the sample shows association of seventeen DMSO molecules with the complex. Some of the solvent molecules are probably trapped inside the spacious cavity.

The same complexation reaction was also carried out in DMSO-d<sub>6</sub> and the solution was directly monitored by NMR spectroscopy. The spectrum obtained matched exactly with that of the isolated complex and reaction goes to completion within 5 min. No peaks other than due to complex 2 were observed that establishes the quantitative self-assembly and remarkable thermodynamic stability of 2.

Finally, the structure of complex 2 was determined unambiguously by X-ray diffraction study.<sup>§</sup> Prismatic crystals suitable for analysis were obtained by slow diffusion of acetone into a DMSO solution of 2. A perspective view of the molecule is shown in Fig. 3. The six Pd(II) ions involved in the structure occupy the apices of an imaginary octahedral array. Trigonal faces of the octahedron are capped by the tripodal non-planar ligands 1, in a truncated fashion leading to a sphere. The plane of central aromatic ring lies 5.2 Å above the plane described by the Pd(II) triangle. The structure of 2 possesses twelve windows on its surface. All the metal centers have square planar geometry with Pd–N bond distances spanning the range of 1.9–2.0 Å.

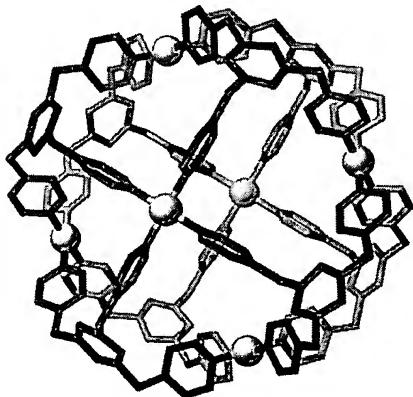


Fig. 3 Representation of  $[(\text{Pd})_6(\text{L})_8]^{12+}$  in the crystal structure of 2.

The giant, hollow structure of the sphere deserves particular attention. The average distance between axially located Pd centers is 15.2 Å and that of equatorial centers is 10.7 Å. The average distance between the central benzene rings of the ligands situated at the terminus of the three-fold axis is 19.2 Å.

In conclusion, the result shows quantitative self-assembly of a hollow, spherical molecule obtained from 14 small and simple components. The important features of the molecular sphere presented here are the extraordinarily large cavity, good solubility in polar solvents, and remarkable stability in solution. The nano-sized dimension of the molecule emphasizes that it is rather a molecular-based nanoparticle without size distribution. Ligand modification is currently under investigation in expectation of new and unique cage structures using the strategy employed here.

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## Notes and references

- † Ligand 1: <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, TMS):  $\delta$  8.969 (d, 6 H, a), 7.722 (d, 6 H, b), 7.542 (s, 3 H, c), 4.432 (s, 6 H, d).
- ‡ Complex 2: <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, TMS):  $\delta$  9.655 (d, 48 H, a), 7.807 (d, 48 H, b), 7.588 (s, 24 H, c), 4.621 (s, 48 H, d). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, TMS):  $\delta$  156.255 (Cq), 151.709 (a), 137.994 (Cq), 132.024 (c), 127.227 (b), 41.018–40.017 (d and DMSO). Anal. Calc. for C<sub>192</sub>H<sub>168</sub>N<sub>36</sub>O<sub>36</sub>Pd<sub>6</sub>(17DMSO): C, 49.15; H, 4.93; N, 9.13%. Found: C, 48.79; H, 4.88; N, 9.45%.
- § Crystal data for 2: C<sub>192</sub>H<sub>168</sub>N<sub>36</sub>O<sub>36</sub>Pd<sub>6</sub> (formula without including solvent molecules),  $M = 4194.13$ , tetragonal, space group  $P4_3/nm$ ,  $a = b = 34.312(4)$  Å,  $c = 29.063(4)$  Å,  $U = 34217(7)$  Å<sup>3</sup>,  $T = 193$  K,  $Z = 4$ ,  $\lambda = 0.71073$  Å, 89663 reflections measured, 11580 unique ( $R_{\text{int}} = 0.1662$ ) which were used in all calculations.  $R_1 = 0.1203$ , and  $wR2 = 0.2800$ . See ESI† for further details. The crystal structure consists of a  $[(\text{Pd})_6(\text{L})_8]^{12+}$  cation, nitrate anions and solvent molecules. However, the anions and solvent molecules were not located definitely due to the solvent dependent nature of the large cavity and high symmetry of the framework. CCDC reference number 189781. See <http://www.rsc.org/suppdata/cc/b2/b206625b/> for crystallographic data in CIF or other electronic format.
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